# Synthesis of New Alternating Block Copolymers with Tailored π-Conjugated Blocks and Non-Conjugated Aliphatic Spacers

## Dissertation

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139 Pages
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31 Schemes

# 1. Introduction and Objectives

The discovery of metal-like conductivity in oxidized poly(acetylene), or shortly after in polyaromatic systems such as poly(pyrrole), poly(thiophene) or poly(aniline) in the late seventies and early eighties (1-6), has progressively generated a rich library of synthetic chemistry in the more general context of functional π-conjugated systems. As for conductive polymers in general, the synthetic chemistry of linearly π-conjugated systems has developed considerably over the past twenty years and has greatly diversified in terms of objectives and methods. In 1990, the realization of the first electroluminescent devices, in which a π-conjugated polymer was used as a lumophore, represents a turning point in the field of π-conjugated systems (7,8). This discovery, together with a parallel intensification of research on field-effect transistors (9,10), photovoltaic cells based on π-conjugated polymers and oligomers (11-13), nonlinear optical materials (14), plastic solar cells (15-19) and optically pumped lasers (20) contributed strongly to build up a different vision of linear π-conjugated systems.

From a synthetic point of view, conjugated polymers are available in a never-ending variety of different chemical structures and topologies. They have a distinct propensity to develop tertiary structures. These tertiary structures are aggregates involving one or several macromolecules, and, depending upon their morphology, can exhibit dramatic differences in the physical and optical properties of different preparations of the same polymer.

The class of conjugated polymers that has commanded the most attention in the past is undoubtedly the poly(p-phenylenevinylene)s (PPVs) which gained popularity since Friend's report of organic polymeric LEDs (7, 21, 22). Other well-established classes of conjugated polymers include the polydiacetylenes (23, 24), polyphenylenes (25, 26) and polyacetylenes (27, 28). However, the closest structural relative to PPV, the poly(phenyleneethylene)s (PPE), have attracted much less attention in the polymer community, despite their fascinating properties. Only recently has the group of Swager (29), Muellen (30), and Weder (31, 32) demonstrated that PPEs with their unique

property profiles are fantastic materials in such diverse areas as explosive detection (29), molecular wires in bridging nanogaps (33 - 38) and polarizers for LC displays. Not only have PPEs themselves found considerable attention, so have their mono dispersed oligomers (39-47).

The electronic properties of conjugated macromolecules are primarily governed by the chemical structure of the polymer backbone itself; but a number of additional tools can be employed to further manipulate the bandgap of conjugated polymers. Control of the effective conjugation length by the introduction of side chains which exhibit steric interactions and force the backbone to twist, along with the design of copolymers that comprise well-defined conjugated segments are illustrative examples of how emission color can be varied over a broad spectrum (48, 53). In the case of PPV, shortening of the effective conjugation length is essential in order to shift the emission spectrum from green to blue. In addition, the improvement of electroluminescence efficiencies due to the introduction of non-conjugated segments in the main chain has been reported (54). Organosilicon moieties or linear aliphatic units have been used to obtain processable conjugated PPV (55-59) and PPP (60, 61). In contrast, there are few examples of PPEs containing non-conjugated spacers in the main chain (62, 63).

Motivated by the above, the goal to arrive at a system where one could easily fine-tune the optical and electronic properties of the said polymers with very little chemical manipulation was established. The main objective of this work centers on the synthesis of new PAE's containing both rigid and flexible units. The subsequent alternating block copolymers have been designed so that one can study the effect of including both conjugated, rigid bipyridine-aromatic units and non-conjugated, flexible alkyl diether units in the main polymeric chain, and their resulting opto-electronic properties. The length of the conjugated moieties, and the length of the non-conjugated moieties in the polymer backbone, and finally the length of the side chains should be varied and their effect on the polymers opto-electronic properties should be investigated.

# 2. General Part

## 2.1 Step-Growth Polymerization

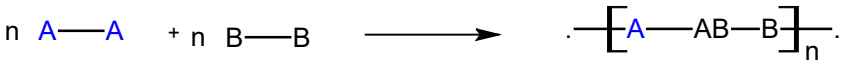
The classical subdivision of polymers into two groups was made around 1929 by W.H. Carothers, who proposed that a distinction be made between polymers prepared by the stepwise reaction of monomers and those formed by chain reactions. The division is as follows:

a) Condensation polymers, where small molecules are eliminated during a reaction.

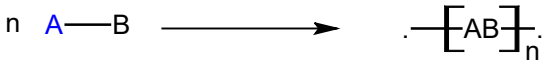
b) Addition polymers, where no such loss occurred.

The term condensation was later changed to a more accurate term of "step-reaction", where the elimination of small molecules is not a requirement.

Two major groups, both distinguished by the type of monomer involved, can be identified in step-growth polymerization. In the first group, two polyfunctional monomers take part in the reaction, each possessing one distinct type of functional group.




The second group is encountered when the monomer contains more than one type of functional group, represented generally as A-B, where the reaction is as follows:



## 2.2 Carothers Equation

W. H. Carothers proposed a simple equation relating the number average chain length $x_n$ to a quantity p describing the extent of the reaction for linear polycondensation or polyaddition.

If $N_0$ is the original number of molecules present in an A-B monomer system, and N the number of all molecules remaining after time t, then the total number of functional groups of either A or B which have reacted is $(N_0-N)$. At time t, the extent of the reaction p is given by:

$$P = (N_0 - N) / N_0 \quad \text{Or} \quad N = N_0 (1-P)$$

If we remember that $x_n = N_0/N$, a combination of this expression gives the Carothers equation in the following form:

$$x_n = 1/(1-p)$$

The Carothers equation is particularly useful when we examine the numerical relation between $x_n$ and p, thus for p = 0.95 (95 % conversion) , $x_n$= 50 and when p= 0.99, then $x_n$= 100.

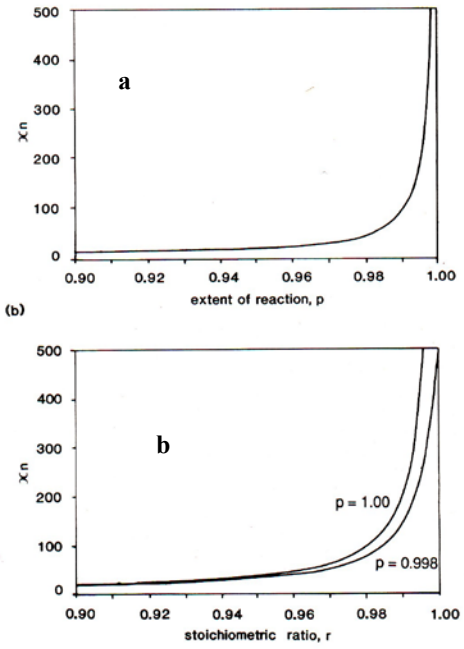



**Figure 1**: Variation of the Degree of Polymerization

The above equation is only valid when the exact stoichiometric ratio of the monomers is known. However, during real step-growth polymerization, the exact ratio of monomers becomes very difficult to determine due to the minute differences in reactivity of the end-groups in the starting materials, decreasing the frequency of functional groups meeting and reacting, as well as interference due to contaminants. In such cases, control of the stoichiometric imbalance is useful. This can be expressed by the modified Carothers equation:

$$x_n = (1+r) / (1+r-2rp)$$

where r is the ratio of the number of molecules of the reactants.

Another important characteristic of step-growth reactions is that their polymerization grade is linear with the reaction times. Therefore, longer reaction times lead to higher conversion.

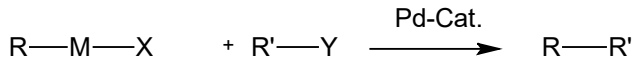
## 2.3 Palladium Catalyzed Cross-Coupling Reactions

### 2.3.1 Pd-catalyzed Reactions in General

Since Kumada and Corriu reported the first cross-coupling reaction in the 1970s (64, 65), transition metal-catalyzed cross-coupling methods have blossomed and have greatly altered the landscape of organic synthetic chemistry (66-69). These methods offer several advantages compared to classical synthetic methodologies.

Magnesium and lithium mediated cross-coupling reactions were the first examples of Pd-catalyzed cross-coupling reactions, **Scheme 1** (64, 65). Although still very effective in many synthetic schemes, the major drawback associated with magnesium reagents in cross-coupling reactions is their lack of chemoselectivity. In contrast, zinc mediated cross-couplings are less reactive and can tolerate many functional groups (70-72). Another important Pd-catalyzed cross-coupling reaction employs organotin reagents. This type of reaction was independently discovered by Migita and Still (73, 74). A distinct advantage of this reaction lies in the mildness of the reaction conditions employed (75-77).

Finally, we arrive at the widely used Pd-catalyzed cross-coupling reaction with borinic and boronic acid derivatives. This reaction is commonly referred to as the Suzuki-Miyaura reaction (78-81). The reaction requires excess base or fluoride to form borates, which are electronically rich, thus facilitating the transmetalation step in the catalytic cycle. Reaction conditions are usually mild and many functional groups are also tolerated.

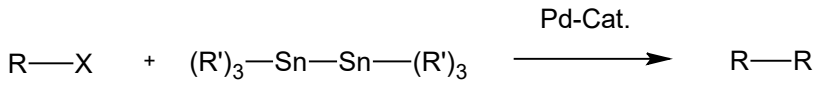



X = Cl , Br, I

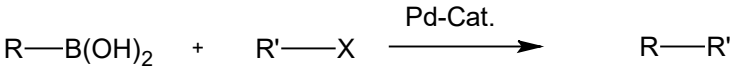
Y = Cl, Br, I

M = Mg, Li, Zn

*Magnesium, lithium and zinc mediated Pd - cross coupling*




*Tin mediated Pd - cross coupling*



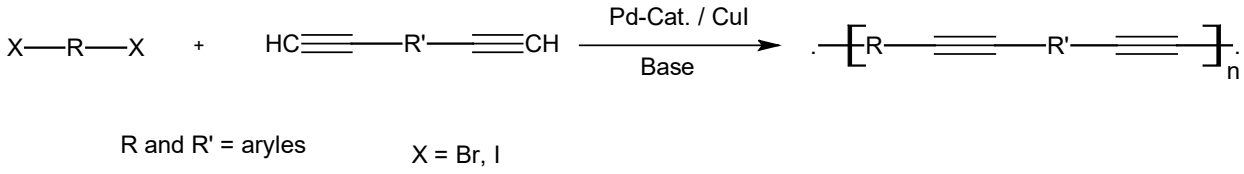

*Boron mediated Pd - cross coupling*

**Scheme 1**: Transition Metal Mediated Pd-cross Coupling Reactions

Compared to the above-mentioned cross coupling reactions, the Pd-cross-coupling reaction forming a $sp^2$-sp carbon bond is one of the mildest and most successful methods known. Reactions involving copper acetylides, known as the Castro-Stephens reaction, are harsh and require a stoichiometric amount of copper (82, 83). Functional group tolerability is also limited in this case and only aryl iodides can be used. The reaction is dramatically improved by the addition of a palladium catalyst. The success of this coupling relies on the higher acidity of the alkynyl proton. Therefore, unlike other methods there is no need to activate the nucleophilic cross-coupling partner. For instance, Nigishi, Suzuki-Miyaura, and Migita-Stille reactions require the preparation of C-Zn, C-B, and C-Sn bonds, respectively, prior to their coupling. Pd-cross-coupling is a very effective method for preparing liquid crystals and conductive polymers. This is, in general, the easiest way to create carbon-carbon bonds, and the resulting triple bond can be readily transformed to other functional moieties.

### 2.3.2 Heck-Cassar-Sonogashira-Hagihara Cross-Coupling

The Heck-Cassar-Sonogashira-Hagihara palladium catalyzed cross coupling reaction of terminal alkynes with aromatic bromides or iodides in amine solvents, using palladium as a catalyst, has been known since 1995. It is probably one of the most frequently used C-C bond forming reactions in organic chemistry (84-86). This cross-coupling forms C-C single bonds between an sp and $sp^2$ hybridized carbon center. In general, dihalogenated aryl or heteroaryl compounds react with terminal diethynyl compounds to form polymers, according to the general reaction in **Scheme 2**.




**Scheme 2**: General Scheme of Heck-Cassar-Sonogashira-Hagihara Palladium-Catalyzed Cross Coupling Reactions

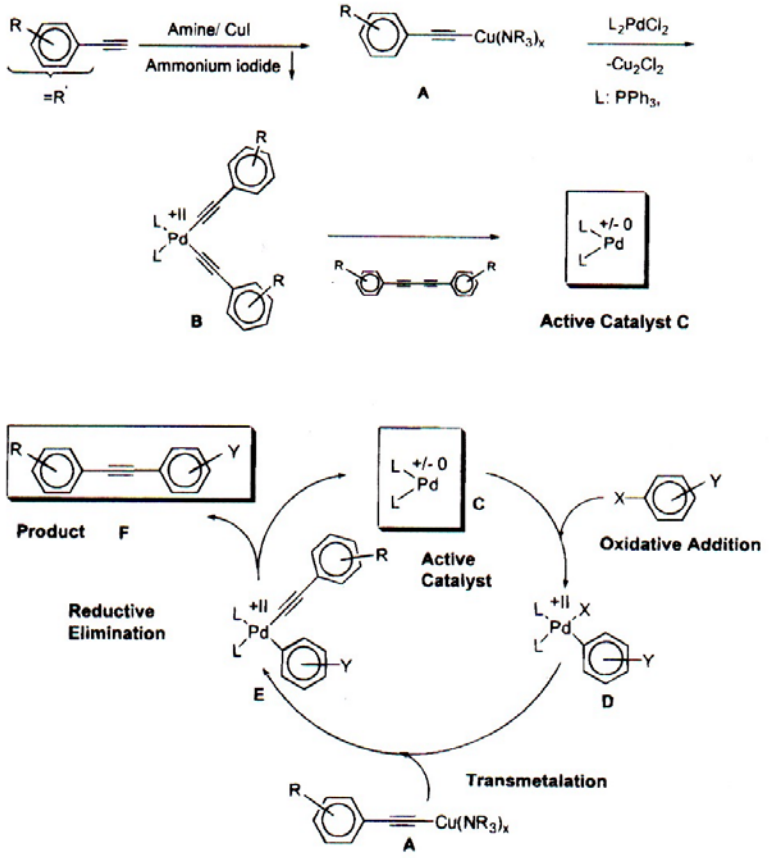
In addition to the monomers, a typical reaction mixture contains several components in analytical amounts. The palladium catalyst in the form of $Pd^0$ $(PPh_3)_4$ or $(Ph_3P)_2PdCl_2$ is the center where the carbon-carbon-bond forming reaction takes place. Most frequently, 0.1-5 mol% of $(Ph_3P)_2PdCl_2$ and various amount of CuI are used in both organic and polymer-forming reactions. With the more reactive iodoarenes, 0.1-0.3% catalyst and CuI should be sufficient for successful conversion. When using $Pd^{2+}$, small amounts of alkyne are converted to diyne in the activation step. It is therefore desirable to add a small excess of the alkyne in order to balance the stoichiometry and obtain high molecular weight polymers. To overcome this problem, some authors have reported using $PPh_3$ to generate in situ $Pd^0$ (87,88). The presence of CuI seems to be necessary for the conversion of dibromoarenes into their corresponding alkynylated products.

In general, the yield and the purity of the coupling products resulting from Heck-Cassar-Sonogashira-Hagihara reactions is very dependent upon the careful choice of amine and co-solvent used. Several papers in the literature describe the effect of different amines on the coupling reactions (89,90).

Di-iodoaryl compounds are advantageous compared to the di-bromoaryls and yield higher molecular weight products with less side reactions, due to milder reaction conditions. The type of substituents on the haloarenes plays a crucial role in the coupling reactions also. It is reported that electron-withdrawing groups accelerate the oxidative addition to the electron rich $Pd^0$ (91). Ortho and para-positioned acceptor substituents are more efficient than those in the meta-position.

### 2.3.3 Mechanism of Heck-Cassar-Sonogashira-Hagihara Cross-Coupling

The mechanism of Sonogashira cross-coupling is still not entirely understood. However, it is assumed that the catalytic cycle is occurring in three main steps, and under the 16/18 valence electron rule (92). In the first step, two molecules of cuprated alkynes transmetalate the palladium catalyst precursor and form B. B is not stable under the reaction conditions used and reductively eliminates a symmetrical butadiyne and creates the active catalyst C. In an oxidative addition step, the aromatic bromide or iodide forms the intermediate D, which after transmetalation with A, leads to the diorganopalladium species E. This species undergoes reductive elimination to the product and reforms the active catalyst C.




**Scheme 3**: The Heck-Cassar-Sonogashira-Hagihara Pd-Cross-Coupling Mechanism

## 2.4 Block Copolymers of Conductive Polymers

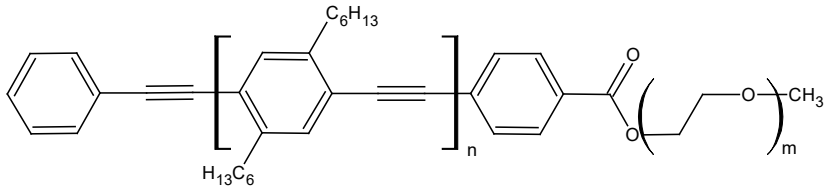
With the introduction of π-conjugated systems in electronic devices and the desire to arrive at molecular electronics based on these systems, the detailed understanding of the supramolecular interactions between the individual π-conjugated molecules has become one of the most challenging areas in synthetic research. Inter-chain electronic coupling determines the performance of π-conjugated based electronic devices. When moving from isolated chains to an intermolecular hierarchy, the charge transfer between chains is required for conduction in a microcrystalline or mesoscopic phase. To arrive at microcrystallinity, it is necessary to have (latent) solubilizing groups. A number of methods to control solubility are known. Whereas side chains are useful at the mesoscopic level of microcrystallization, they are sometimes detrimental for macroscopic ordering (93-100). It is evident that materials research in the area of semiconducting polymers is only useful when macromolecular engineering by organic synthesis is combined with investigations to control molecular architecture at all levels of hierarchy.

The morphology of polymers has been controlled mainly by synthesizing defined block copolymers (101). The microphase separation of diblock polymers depends on the total degree of polymerization, the Flory-Huggins χ parameters, and the volume fraction of the constituent blocks. The segregation product χN determines the degree of microphase separation, with higher values giving stronger segregation. By replacing one of the segments with a π-conjugated rigid unit, a rod-coil diblock polymer is obtained (102-115). The self-assembly of these polymers is also affected by the aggregation of the π-conjugated segments. Furthermore, the stiffness asymmetry present in rod-coil diblock polymers results in an increase in the Flory-Huggins χ parameter. As a consequence, phase separation can already occur at lower molecular weights and for rigid segments consisting of π-conjugated oligomers. In addition to the self-assembly induced by block copolymer design, the processability of these polymers is the second main advantage.

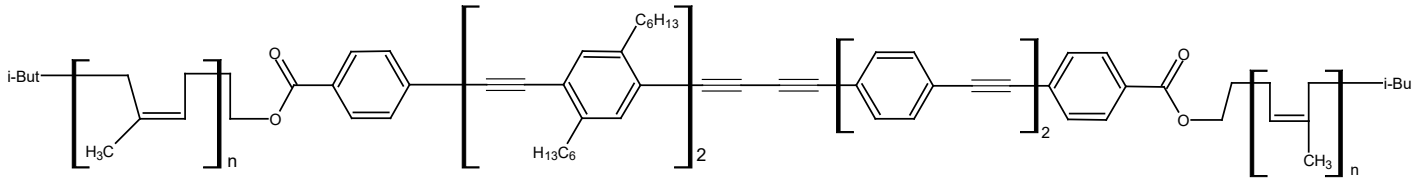
### 2.4.1 Block Copolymers of Poly(aryleneethylene)s

One way to manipulate the supramolecular structure and the processablity of a polymer is to incorporate a conjugated rod into a rod-coil molecular architecture. The structural manipulation of the conjugated rods is of paramount importance in achieving efficient opto-physical properties in solid state molecular structures.

Rod-coil copolymers consisting of poly(p-phenyleneethylene) as the rod block and poly(ethylene oxide) as the coil block were prepared (113), **Scheme 4 A**. More recently, the synthesis of triblock poly(isoprene-block-p-phenyleneethylene-block-isoprene) was reported by Godt et. al (114).




A

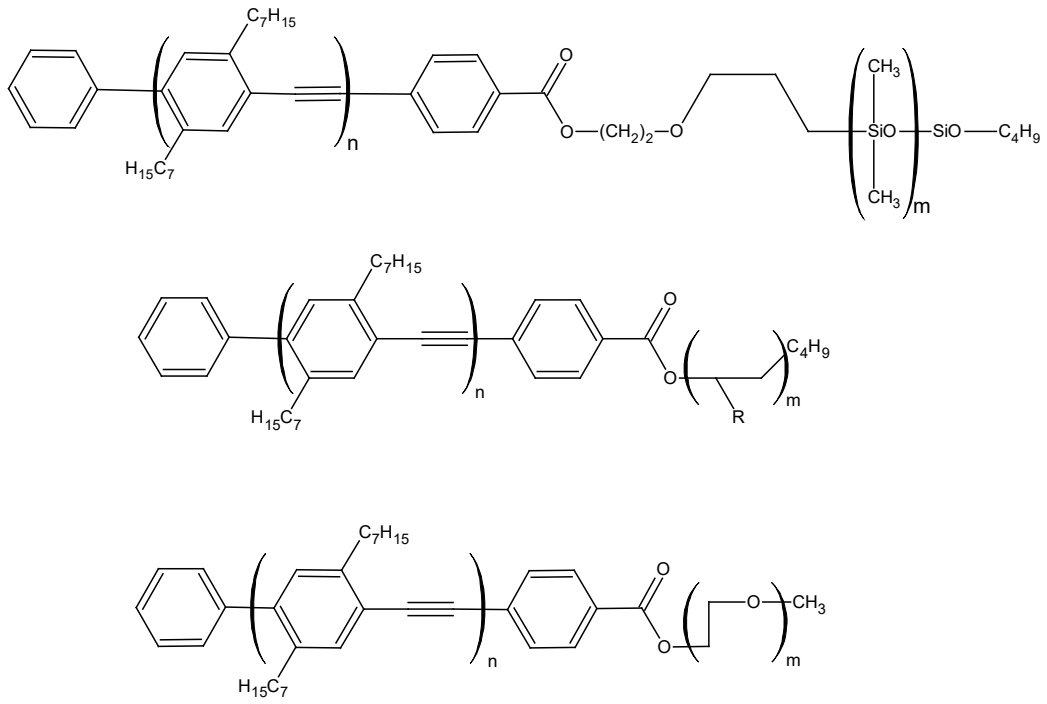



B

**Scheme 4**: Di-block (A) and Tri-block (B) Rod Coil Copolymers

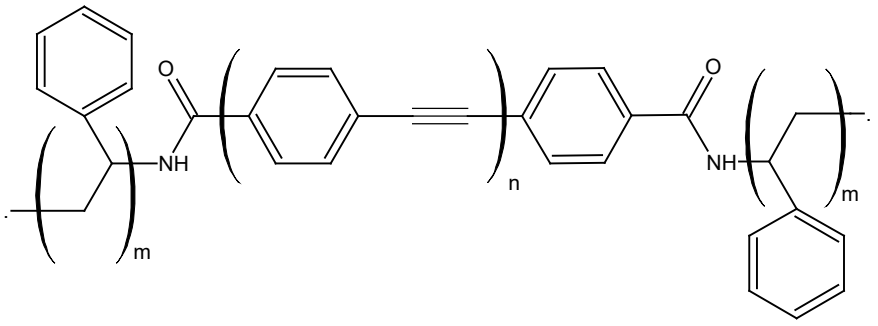
Lazzaroni et. al. showed that rod-coil copolymers, containing poly(p-phenyleneethylene) as the rod segment, have a strong tendency to spontaneously assemble into stable, ribbon-like fibrillar morphologies when coated on mica substrates (115, 116).

The synthesis of block copolymers consisting of polydimethylsilane or poly(ethyleneoxide) as the coil segments with rod segments of poly(p-phenyleneethylene), were carried out by Muellen et. al. (117-119), **Scheme 5**. Optical measurements showed the influence of the coil blocks on the opto-electronic properties of the rod segments by induced phase separation.




**Scheme 5**: AB-block Copolymers

Triblock copolymers of oligo(p-phenyleneethylene) were also synthesized (120, 121). In these cases phase separation was observed in poor solvents, **Scheme 6**.

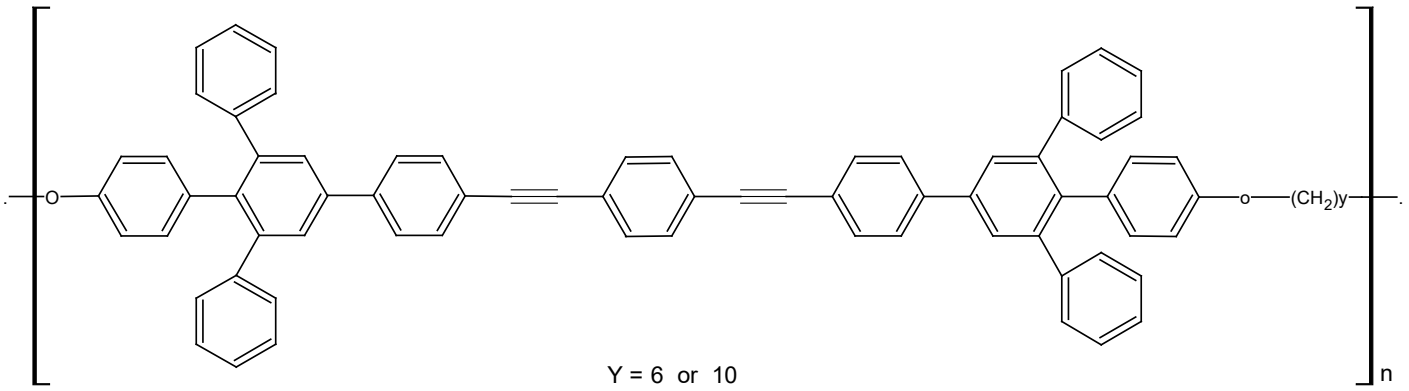



**Scheme 6**: Tri-block Copolymers with Amide Structure

### 2.4.2. Alternating Block Copolymers of Poly(p-phenyleneethylene)s

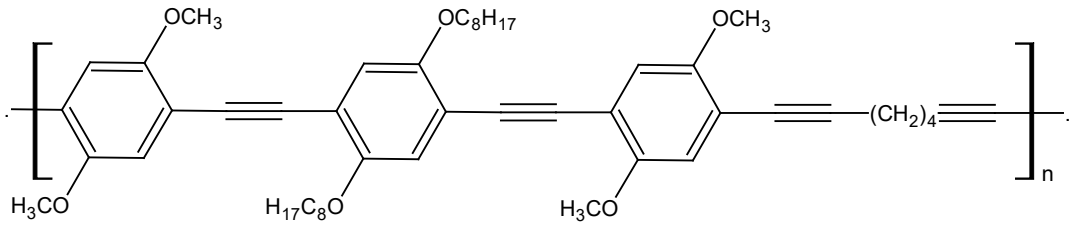
The preparation of alternating rigid, conjugated poly(p-phenyleneethylene) and non-conjugated aliphatic spacers is seldom observed in the literature. Such unique structures will allow the chemist to control the length of the conjugation resulting in polymers with well-defined lumophores. In the case of PPV, shortening of the effective conjugation length is essential in order to shift the emission spectrum from green to blue. In addition, the improvement of electroluminescence efficiency, due to the introduction of non-conjugated segments in the main chain have been reported [54].

Spiliopoulos et. al. synthesized polyethers that contain alternating rigid PPE (122), **Scheme 7**. The polymers showed enhanced solubility in organic solvents with high thermal stability. They displayed pure blue light emission and their photoluminescence maxima are strongly blue-shifted, meaning that the aliphatic spacers of these polymers affected the UV-Vis absorption and emission in different ways.




**Scheme 7**: Alternating AB Block Copolymer with Ether Structure in the Main Chain

Weder and coworkers prepared an alternating copolymer with alkoxy substituted PPE-copolymer segments with $C_5$-aliphatic spacers, **Scheme 8** (123). The segmented polymer was found to have an absorption that is blue-shifted by more than 60 nm when compared to the alkoxy-substituted PPEs and also exhibits a significantly blue-shifted emission when compared to the latter. It was reported that the emission spectra of these polymers show well-resolved vibronic features. The authors also reported that the modification of the PPE backbones results in a more pronounced wavelength shift in absorption compared to the shift observed in emission.




**Scheme 8**: Alternating AB Block Copolymers with Aliphatic Chains in the Polymer Backbone

E. Klemm has reported the synthesis of a large number of new poly(p-phenyleneethyne)s and phenylene-ethynylene/phenylene-vinylene hybrid polymers with novel properties. The first alternating PPV/PPE hybrid copolymer was synthesized by Klemm and Egbe in 2001. Following this, many novel PPE/PPV copolymers were developed for application in plastic solar cells (124-130). A new class of PPEs, containing bipyridine units in the backbone, were also prepared (131-135).

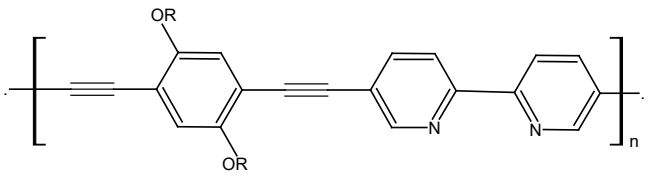
Klemm et. al further incorporated ruthenium metal into the bipyridine containing polymers with the ultimate goal of producing novel polymers with non-linear optical properties (136- 139). Recently, Klemm published the synthesis of new PPEs with electron–deficient aryleneimide units (140), as well as hetero-PPEs with benzodithiazole /quinoxaline/ thiophene units (141).

As an extension of Klemm's work, new alternating block copolymers (of the PAE type) have been synthesized. These polymers have been designed so that deliberate modifications made to their conjugated and non-conjugated segments can be performed in order to produce tailored band gaps, leading to "fine-tunable" absorption and emission maxima in the resulting polymers. The length of the rigid, conjugated bipyridine block (b) will be varied, along with the length of the flexible, non-conjugated spacers (R'). In addition, the length of the alkyl side chains (R), located on the conjugated moieties, will be varied to yield polymers of length n.

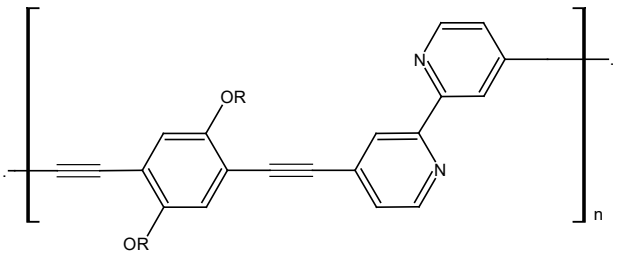
# 3. Results and Discussion

## 3.1. Polymer 15

Poly(p-phenyleneethylene) with bipyridine units in the polymer backbone has been extensively studied by the Klemm group (131-135). Two main polymer structures were synthesized. The first polymer structure is the linear form, incorporating 5,5'-dibromo-2,2'-bipyridine as a monomer (**Scheme 9 A**). The second polymer-type is the zig-zag form, employing 4,4'-dibromo-2,2'-bipyridine (**Scheme 9 B**). These types of PAEs were found to be thermally stable and exhibit high fluorescence quantum yields. In addition, the presence of the bipyridine unit in the main chain allowed for the preparation of polymers having the ability to chelate transition metals along the polymer backbone.



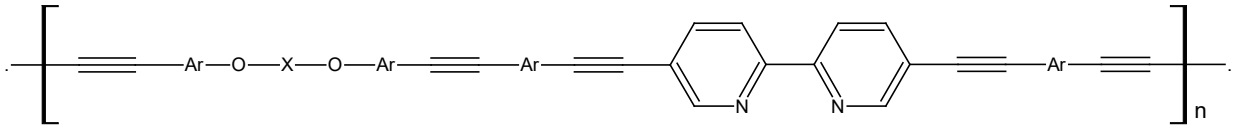

**A**




**B**

**Scheme 9**: Bipyridine-Containing PAE Polymers with Linear and Zig-Zag Backbone (Klemm et. al. (131-135))

It was therefore interesting to prepare new alternating copolymers containing bipyridine units and alkoxy-substituted aromatics in the conjugated rigid blocks, along with non-conjugated aliphatic spacers according the general structure shown in **Scheme 10**.

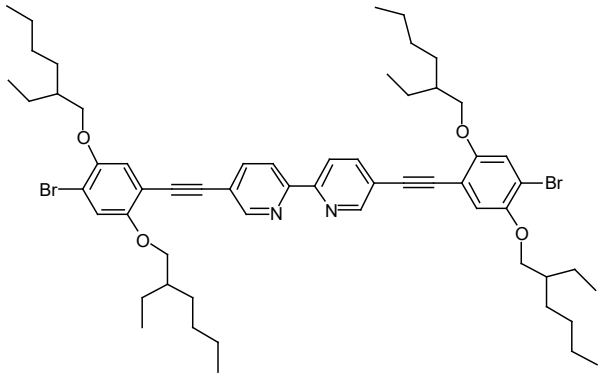



**Scheme 10**: General Structure for Alternating PAE Block Copolymers

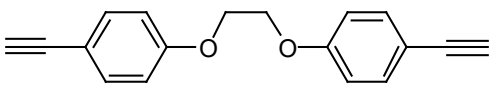
The presence of defined conjugated units in the polymer backbone will allow for the synthesis of novel polymers with blue-shifted absorption and emission maxima. In addition, the introduction of a non-conjugated spacer in the main chain improves the electroluminescence efficiency of the polymer (54).

### 3.1.1 Synthesis of Starting Materials for Monomer 14

The generation of the first alternating copolymer **(Scheme 10)** requires the synthesis of monomer **7** and monomer **14** (**Scheme 11**).



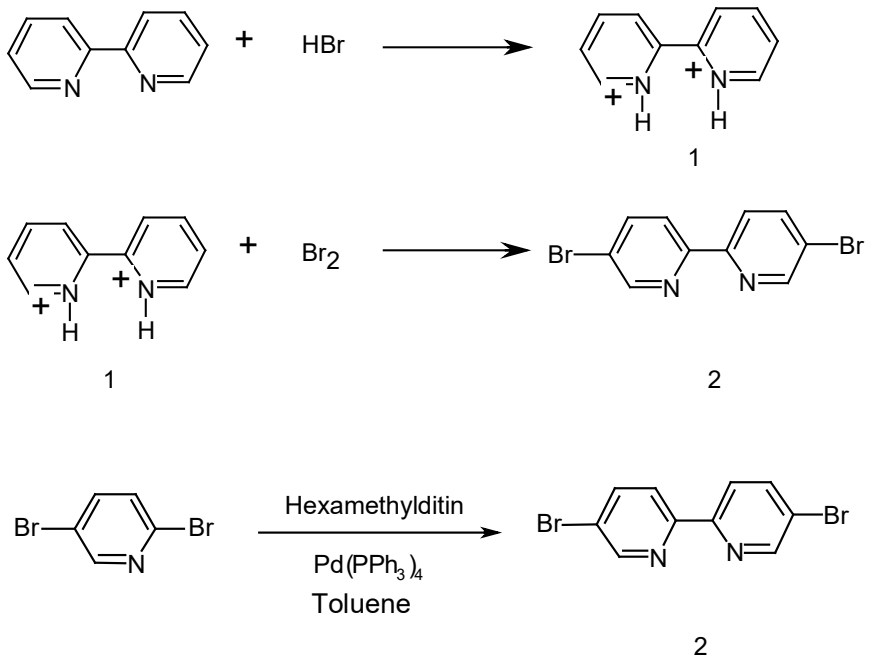

**14**




**7**

**Scheme 11**: The Dibromo and Diacetylene Monomers for the Synthesis of Polymer **15**

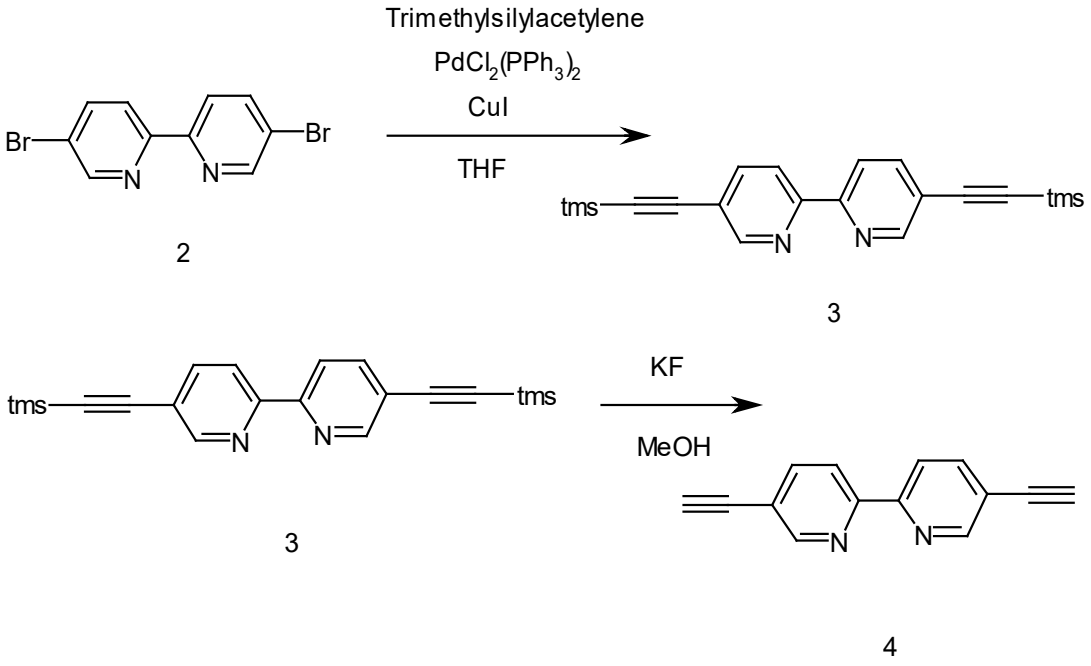
The starting point for the synthesis of monomer **14** was the preparation of 5,5'-dibromo-2,2'-bipyridine (**2**). This compound was first prepared from the 2,2'-dipyridyl dihydrobromide salt (**1**) and bromine in a high-pressure bomb at 190 $^0$C. After 80h, the product was isolated and purified using column chromatography (**Scheme 12**). It was found that the yield of this reaction is relatively low (i.e. less than 30 %), the reaction times are long (i.e. greater than 72 hours), and the work-up is time consuming and cumbersome (142).




**Scheme 12**: Two Synthetic Routes to 5,5'-dibromo-2,2'-bipyridine

Another procedure, developed by Sauvage *et. al.,* was performed (143). In this procedure the dibromobipyridine compound (**2**) was prepared from 2,5-dibromopyridine and hexamethylditin in the presence of $Pd(PPh_3)_4$ in toluene at 90 $^0$C. The yield of this one-step reaction was found to be relatively high (i.e. 80%) and required less preparation time. The dibromobipyridine compound (**2**) was reacted with four equivalents of trimethylsilylacetylene in the presence of a Pd-catalyst, according to Sonogashira Pd-cross coupling reaction conditions (144). The trimethylsilyl-protected bipyridine (**3**) was

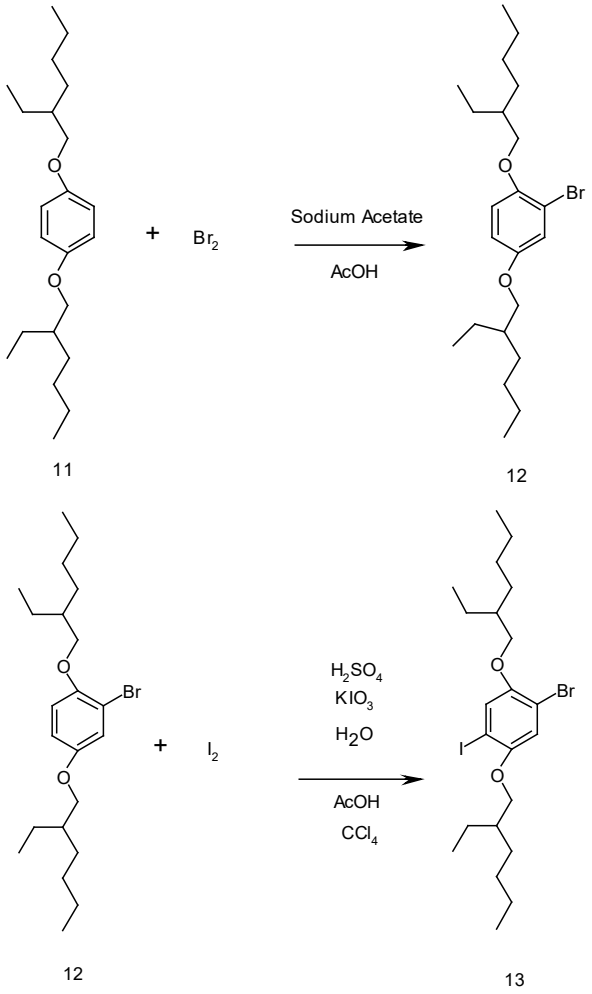
isolated as an off-white powder in 65 % yield (post-column). The deprotection of this intermediate was carried out in a methanol/THF solution at room temperature in the presence of potassium fluoride (**Scheme 13)**. The addition of tetrahydrofuran was found to be necessary for complete solubility. The resulting 5,5'-diethynyl-2,2-bipyridne compound **(4)** was isolated and purified by column chromatography. The $^{1}$H-NMR of Compound **4** clearly shows the characteristic acetylene proton at $\delta$ = 3.31 ppm and the characteristic peaks of the bipyridine rings in the range of $\delta$ = 7.9 ppm to $\delta$ = 8.76 ppm.




**Scheme 13:** Introduction of TMS-acetylene into Compound **2** and its Deprotection to 5,5'-diethynyl-2,2-bipyridine **(4)**

The other molecule required in order to prepare monomer **14** is the dialkoxybromoiodobenzene compound **13** (**Scheme 14)**. Hydroquinone was reacted with two moles of 2-ethylhexylbromide in the presence of potassium hydroxide to yield 1,4-bis(2-ethylhexyl)oxybenzene (**11**) in 85% yield. The dialkoxybenzene **(11)** was mono-brominated in glacial acetic acid to give 2-bromo-1,4-bis(2-ethylhexyl)oxybenzene (**12**).

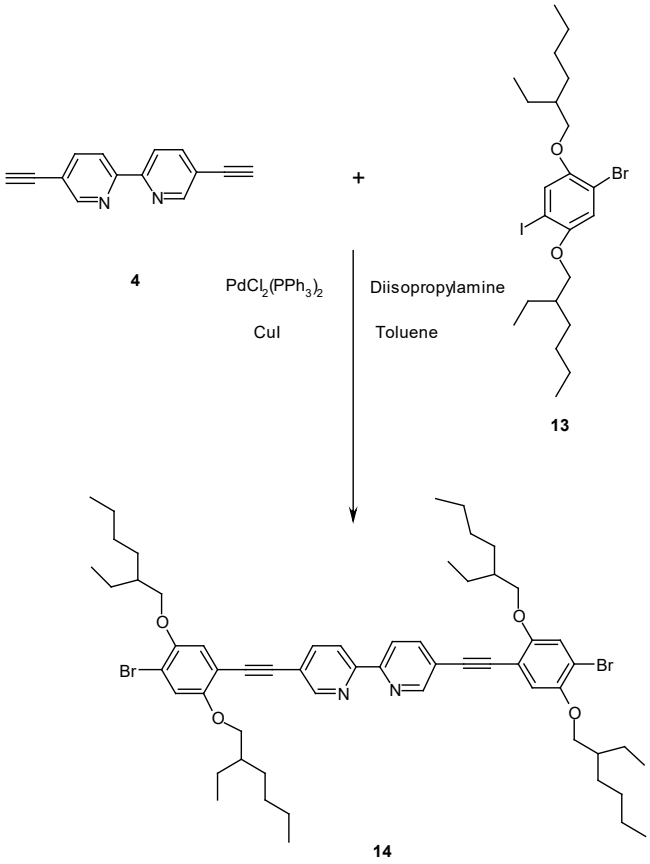
The mono-brominated compound was purified via distillation under high vacuum. This compound was further converted to the iodo-bromo compound (**13**) by reacting with potassium iodate and iodine in acetic acid/sulfuric acid at 120 $^0$C. In order to achieve efficient iodation, several milliliters of carbon tetrachloride were added to redissolve the iodine sublimed during the reaction. The final iodo-bromo compound was purified by distillation under high vacuum. The $^1$H-NMR of the final compound (**13**) shows two distinct singlets at $\delta$ = 6.98 ppm and $\delta$ = 7.27 ppm, representing the aromatic protons, and a doublet for the alkoxy-ether $CH_2$ protons at $\delta$ = 3.80 ppm. The elemental analysis and the mass spectrum further confirm the structure of the desired molecule.




**Scheme 14**: Synthesis of 2-bromo-5-iodo-1,4-bis(2-ethylhexyl)oxybenzene

### 3.1.2 Preparation of Monomer 14

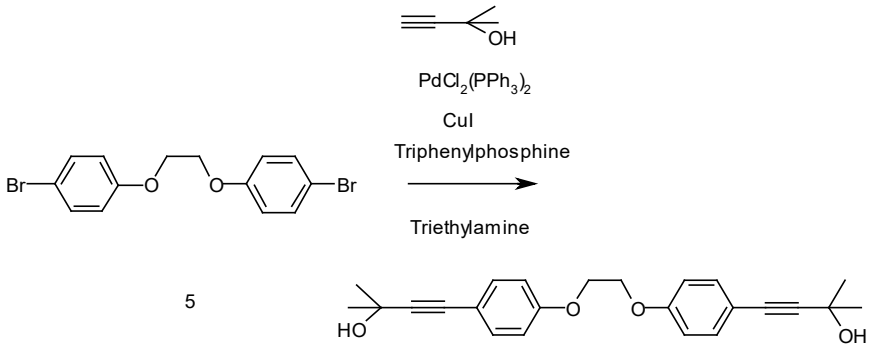
In order to arrive at monomer **14,** 2.1 moles of the alkoxy-bromo-iodo-benzene compound (**13**) were reacted with one mole of bipyridine diacetylene (**4**) according to Sonogashira Pd-cross coupling reaction conditions. The reaction was carried out in freshly dried and degassed toluene, with diisopropyl amine as the base and copper iodide as the co-catalyst. The diacetylene moiety of the bipyridine unit is highly reactive in comparison to the corresponding aromatic unit, due to the electron-withdrawing effect of the nitrogen atoms in the rings. Therefore, the reaction was carried out at 0 $^0$C for the first 3 h, then allowed to react overnight at room temperature in order to avoid further substitution of the bromine atoms. The reaction mixture was worked up and the final product was purified using column chromatography.



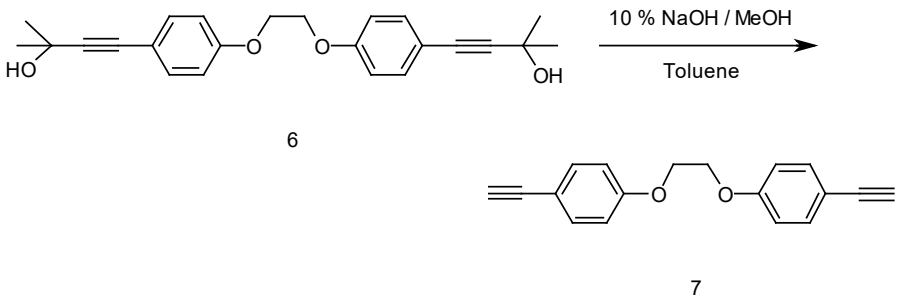

**Scheme 15**: Synthesis of Monomer **14**

### 3.1.3 Preparation of Monomer 7

The preparation of monomer **7** began with the reaction of 4-bromophenol and dibromoethane in water, in the presence of excess sodium hydroxide (**Scheme 16)** (145). Upon boiling and stirring for 10 h, the reaction mixture was allowed to cool to room temperature and the resulting white precipitate was filtered, washed with water, and finally recrystallized from ethanol. The preparation of the diacetylene compound was carried out using 2-methyl-3-butyn-2-ol (MBI) rather than the widely used trimethylsilylacetylene (TMSA). The advantage of using MBI versus TMSA lies in its relatively low price, along with the possibility of conducting reactions at high temperatures without the use of an autoclave. The deprotection of the di-alcohol intermediate (**6**) was carried out in toluene and 10% sodium hydroxide in methanol. The reaction was deemed complete after several partial distillations of toluene. The final diacetylene compound (**7**) was obtained as a white solid after purification by column chromatography. The $^{1}$H-NMR of the final diacetylene compound shows the acetylene protons at $\delta$ = 2.95 ppm and the alkoxy-ether $CH_2$-bridge protons at $\delta$ = 4.26 ppm. The final structure was confirmed by mass spectrometry.




5 6



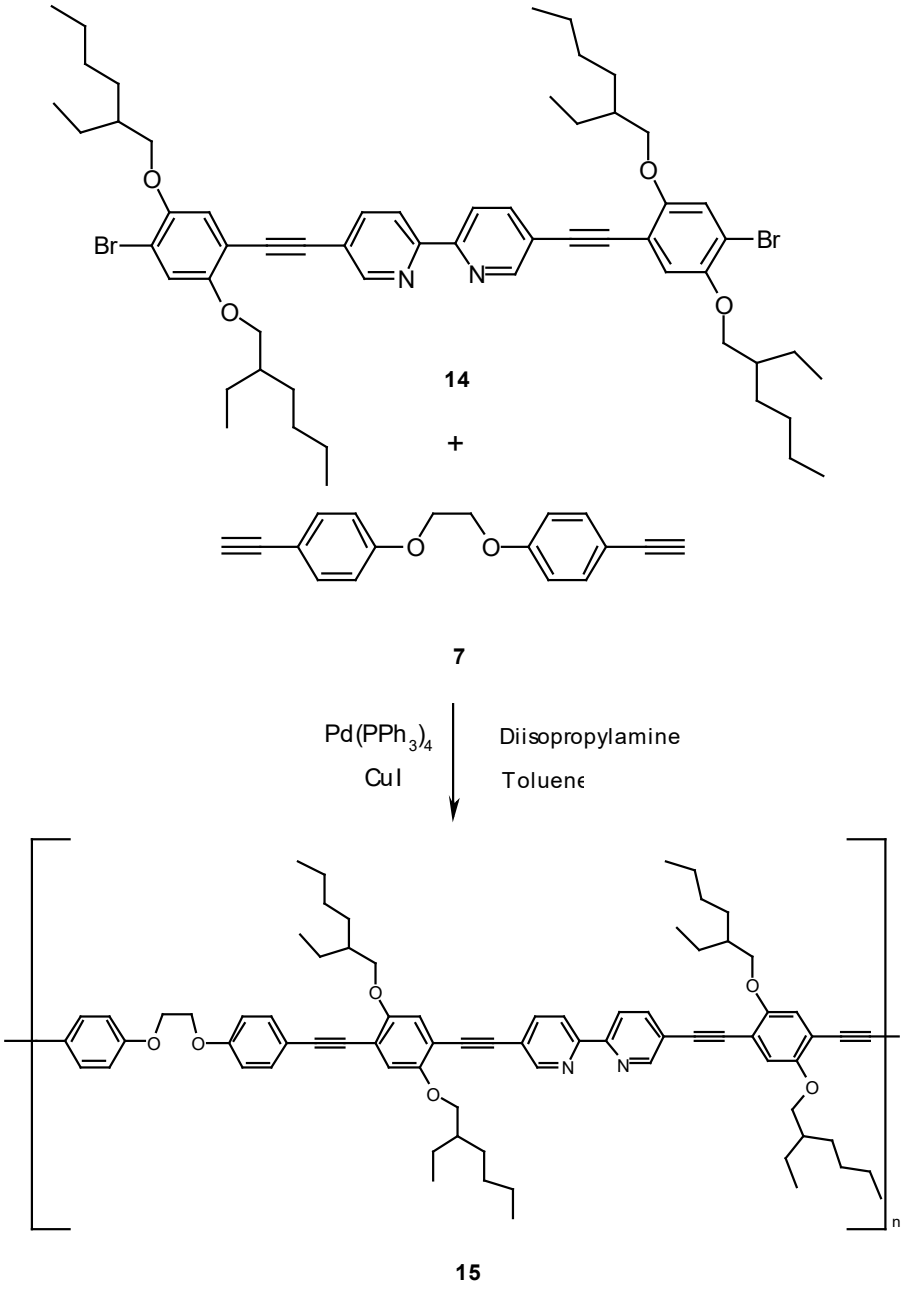

**Scheme 16**: Synthesis of 1,2-bis(4-ethylphenoxy)ethane (**7**)

### 3.1.4 Synthesis of Alternating Copolymer 15

The Sonogashira palladium coupling reaction has proven to be the method of choice in order to synthesize a wide variety of PAEs (20). Giesa was the first to successfully prepare soluble PPE derivatives (146). The attachment of long-chained alkoxy groups to the linear, rigid, PPE backbone was expected to furnish polymers with increased solubility. The choice of alkoxy groups incorporated was based upon the simplicity of the synthesis required to arrive at the corresponding monomers.

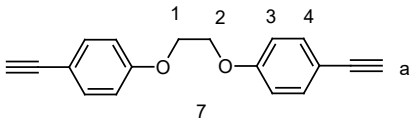
Another way of increasing the solubility of a polymer is to introduce aliphatic spacers in the polymer backbone. In addition to the increase in solubility, the introduction of aliphatic spacers leads to new alternating copolymers with entirely different physical and, most importantly, new optical properties. The introduction of non-conjugated spacers into the polymer backbone makes it possible to synthesize polymers with tailored conjugation that could have defined lumophores and high electroluminescence efficiency. It was interesting for us to therefore synthesize the alternating copolymer (**15**). In order to have sufficient conjugation along the polymer backbone, monomer **14** was synthesized with bipyridine units connected to two aromatic rings via C-C triple bonds from both sides. A branched alkoxy group (ethylhexyl group) was selected in order to increase the solubility of the resulting polymer. For the aliphatic spacer, a diacetylene compound with an alkoxy ethyl group between the two unsubstituted aromatic rings was synthesized.

The polymerization reaction (**Scheme 17**) was carried out in toluene at 75 $^{0}$C. Tetrakistriphenylphosphine palladium was used at a concentration of 4 mol % as the catalyst. This form of catalyst proved to be efficient during the polymerizations performed, producing higher molecular weight polymers than the $Pd^{+2}$ chloride catalyst. In addition, the ratio of the monomer could be kept at 1:1 while a slight excess of the diacetylene compound is usually required when using the $Pd^{+2}$ catalyst. CuI, the co-catalyst, was added at a concentration of 4 mol % in the presence of the diisopropyl amine base. After 68 h, the polymer was isolated by water/toluene extraction. The polymer was subsequently purified by re-precipitation from excess cold methanol. In order to remove the low molecular weight molecules and possible salts present in the crude polymer mixture, the polymer was subjected to an extraction with methanol for 72 hours using the Soxhlett technique. The resulting polymer was found to be very soluble in common solvents such as methylene chloride, DMSO, and toluene. The $^{1}$H-NMR and $^{13}$C-NMR of the polymer in comparison to the starting monomers are illustrated in **Figure 2** and **Figure 2A** of the Appendix, respectively. The spectra clearly show the incorporation of two monomer units in the polymer chain. The $CH_2$-groups in the alkoxy side chains appear at $\delta$ = 3.94 ppm and next to this signal is the $CH_2$-protons of the aliphatic spacer in the polymer backbone at $\delta$ = 4.37 ppm. The integration ratio of the two groups was found to be 1:2, confirming the alternating structure of the polymer chain. The $^{1}$H-NMR does not show any acetylene proton, indicating the absence of acetylene endgroups. The $^{13}$C-NMR shows, as expected, the C-C-triple bond carbons in the range of $\delta$ = 80-96 ppm. The elemental analysis of the polymer shows the presence of 3.5 % bromine. This can be explained by the presence of bromine endgroups in the polymer chain. Unfortunately, such endgroups could not be detected by NMR-spectroscopy.




**Scheme 17:** Polymerization Reaction of Monomer **14** and **7** to Yield Alternating Copolymer **15**

The molecular weight of Polymer **15** was determined by GPC using polystyrene as a reference and THF as the eluent. The number average molar mass was found to be 8,735 g/mol and the weight average molar mass was 15,470 g/mol. The polydispersity index of the polymer was found to be 1.77.

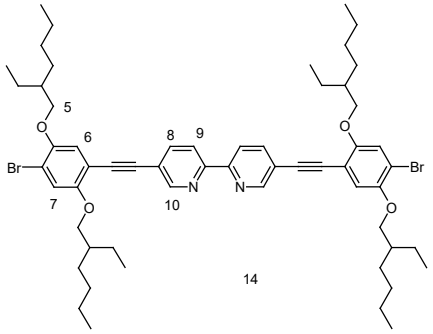



a

1,2

4

3

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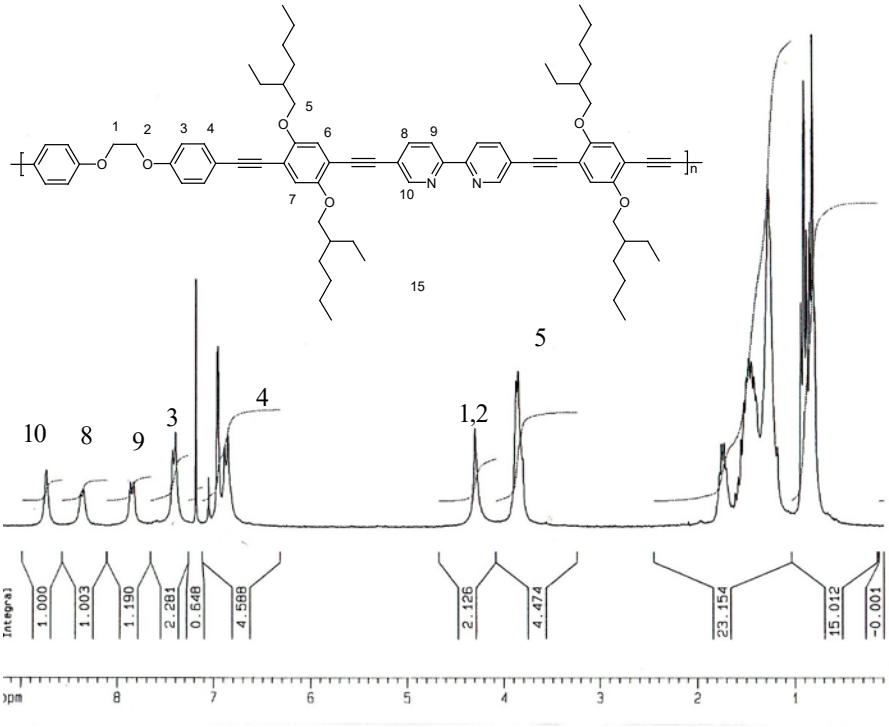



**Figure 2**: The $^{1}$H-NMR of Polymer **15** Compared to Monomer **7** and **14**

The photophysical properties of the polymer were investigated by UV-Vis and Fluorescence spectroscopy (in Methylene Chloride). The absorption spectrum of the polymer is illustrated in **Figure 3**. The absorption maximum of this polymer with the non-conjugated spacer exhibits a hypsochromic shift compared to the fully conjugated polymers with similar bipyridine backbone structures (**Scheme 9**) (131). The UV-absorption shows an additional two small maxima at 349 nm and 319 nm. The absorption maxima at short wavelengths could be assigned to the aromatic and bipyridine rings, while absorption at long wavelengths is attributed to the electron transition $\pi$- $\pi^*$ along the conjugated rigid block.

The photoluminescence spectrum of polymer **15** (**Figure 3A**) was recorded in methylene chloride. The observed blue-shifted emission of this polymer compared to the fully conjugated polymers with bipyridine units suggests an efficient interruption of the conjugation by the aliphatic ether units in the backbone.

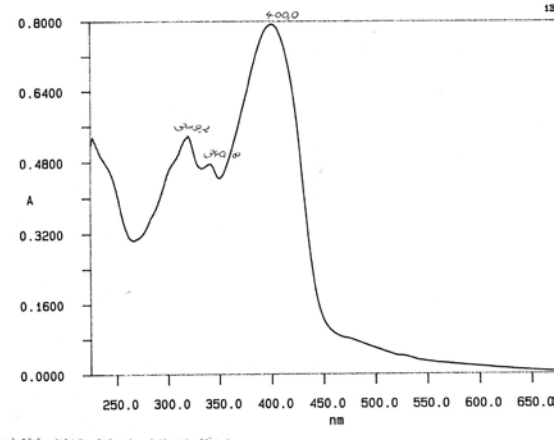



**Figure 3**: UV-Vis Spectrum of Polymer **15** in Methylene Chloride

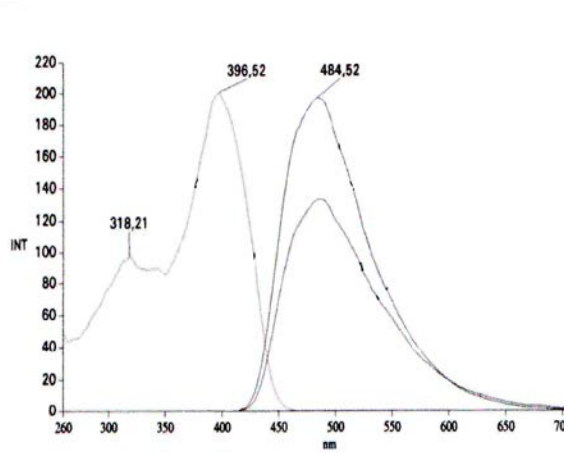
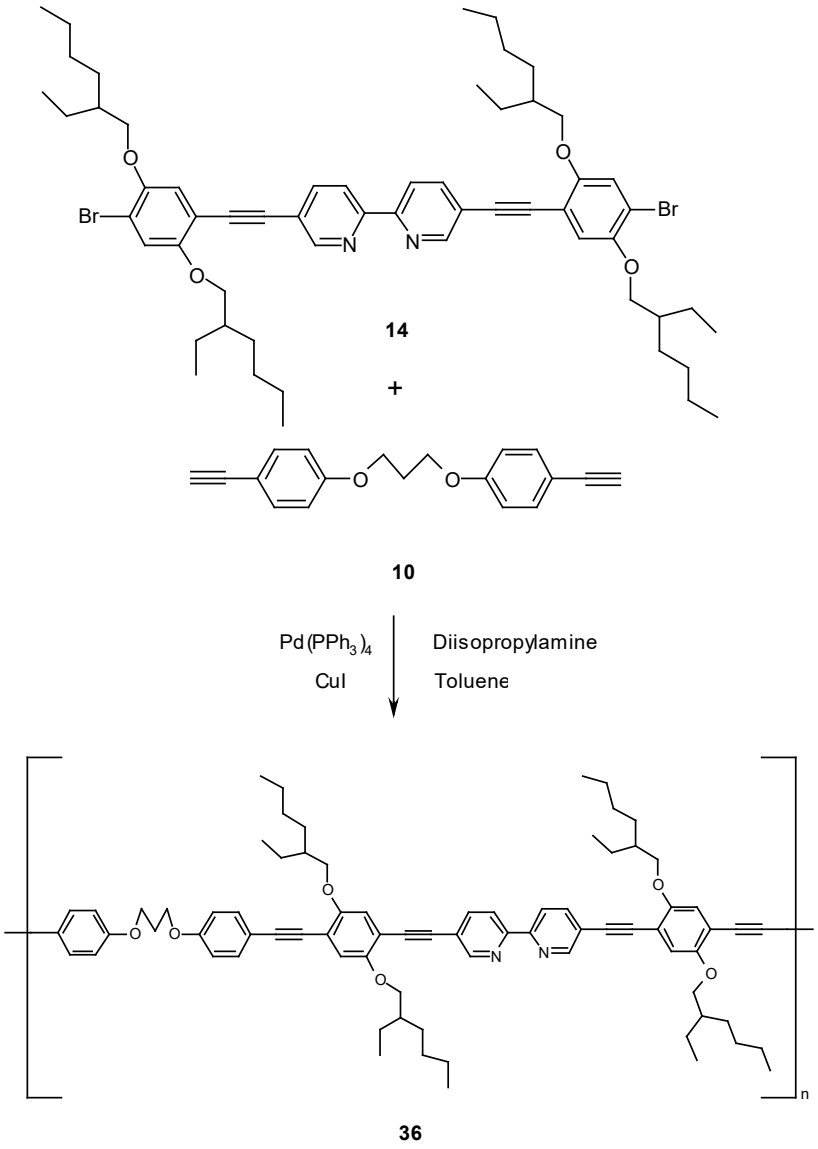



**Figure 3A**: The Fluorescence Spectrum of Polymer 15 in Methylene Chloride

To further investigate the effect of the chain length of the aliphatic spacer in the polymer backbone on the physical and optical properties of the polymer, polymer **36** with $C_3$ chain length was synthesized. It was expected that the length of the aliphatic spacer could have a significant effect on the polymer's flexibility and consequently on the macromolecular arrangement of the polymer chains. The ordered arrangements of the macromolecules could lead to new energy transitions and transfer between the polymer chains. Such interactions will be expressed as new and unique optical properties.

Polymer **36** was synthesized from monomer **10** and monomer **14** in a molar ratio of 1:1 (**Scheme 18)**. The reaction was carried out in toluene using tetrakistriphenylphosphine palladium as the catalyst, copper iodide as the cocatalyst, and diisopropylamine as the base. After 68 h of heating at 75 $^0$C, the polymer was extracted with toluene/water and precipitated from cold methanol. The final purification was carried out by Soxhlett extraction with methanol.




**Scheme 18**: Reaction of Monomer **14** and Monomer **10** to Yield Polymer **36**

The $^{1}H$ and $^{13}C$-NMR spectra of the polymer compared to the two starting monomers are illustrated in **Figure 4** and **Figure 4A** in appendix, respectively. The aliphatic ether $CH_2$ protons of the aromatic side chains and the $CH_2$-ether of the aliphatic spacer in the polymer backbone appear at $\delta$ = 3.91 ppm and $\delta$ = 4.18 ppm, respectively. The $^{13}C$ signals of the C-C triple bond carbons are in the expected range of $\delta$ = 80-96 ppm.

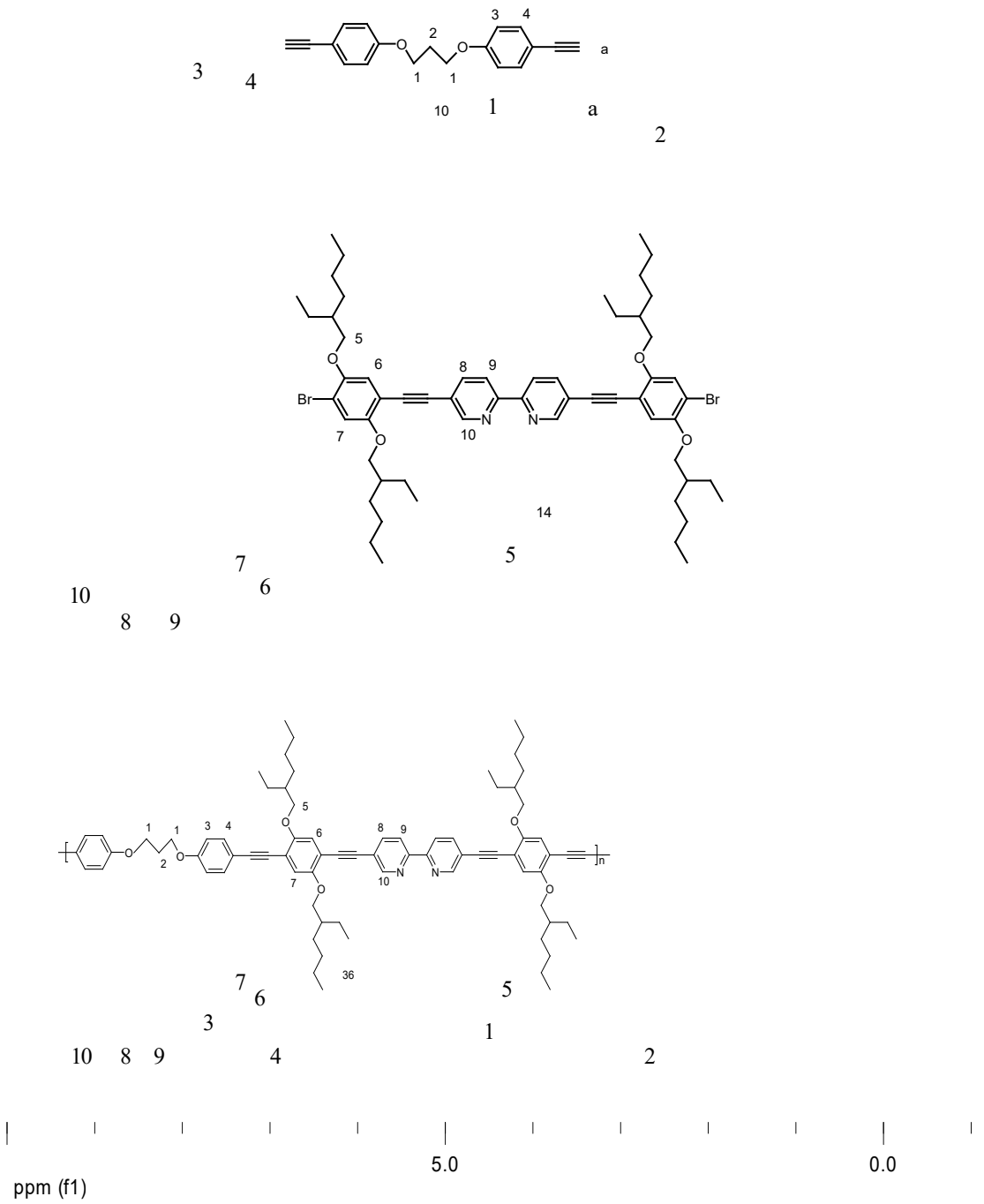



**Figure 4**: $^{1}$H-NMR of Polymer **36** Compared to Monomers **10** and **14**

The molecular weight of the polymer was determined by GPC using polystyrene as the reference. The number average molar mass was found to be 12,005 g/mol and the weight average molar mass was 21,393 g/mol. The polydispersity index of the polymer was found to be 1.78. The molecular weight and the dispersity index of this polymer is similar to the polymer with the $C_2$-chain length, polymer **15**.

The UV-Vis spectrum of this polymer is illustrated in **Figure 5**. The spectrum shows four small maxima at 288, 302, 321 and 344 nm, which could be attributed to the bipyridine and aromatic rings. It is also interesting to note that the absorption maxima at the short wavelengths in this polymer are more pronounced and well resolved in comparison to polymer **15** with the $C_2$ aliphatic spacer. One possible explanation for this phenomenon is that the $C_3$ aliphatic provides more flexibility to the polymer backbone, which in turn leads to macromolecular arrangements in solution, allowing for more transitions between the chains.

The photoluminescence spectrum of polymer **36** is illustrated in **Figure 5A**. The emission spectrum of polymer **36** with the $C_3$ aliphatic spacer shows a maximum at 479 nm and has vibronic bands. The vibronic feature of the emission spectrum could be attributed to the emission from localized excited states to the segments that represent low energy states (147).

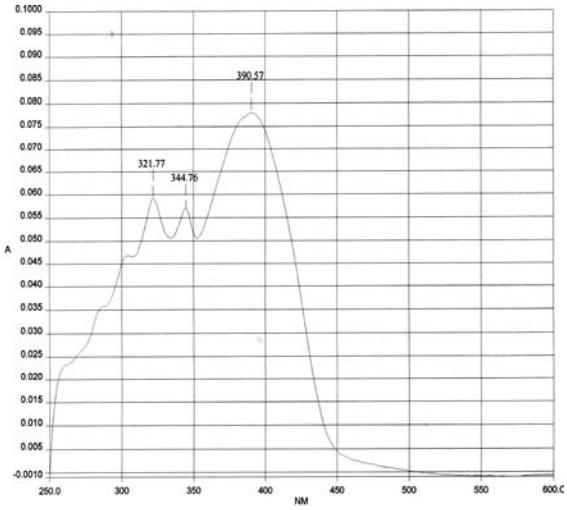



**Figure 5**: The UV-Vis Spectrum of Polymer **36** in Methylene Chloride

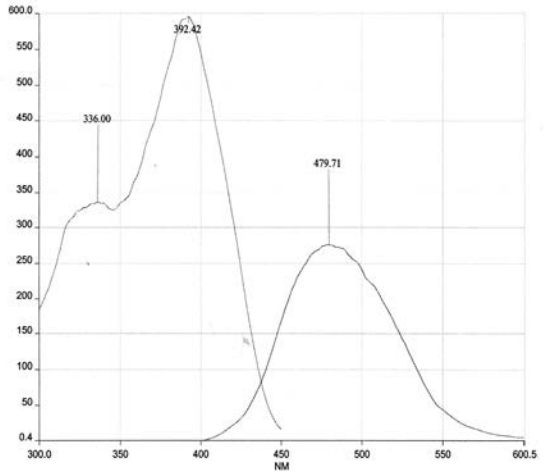



**Figure 5A**: The Fluorescence Spectrum of Polymer **36** in Methylene Chloride

## 3.2 Polymer 44 and Polymer 45

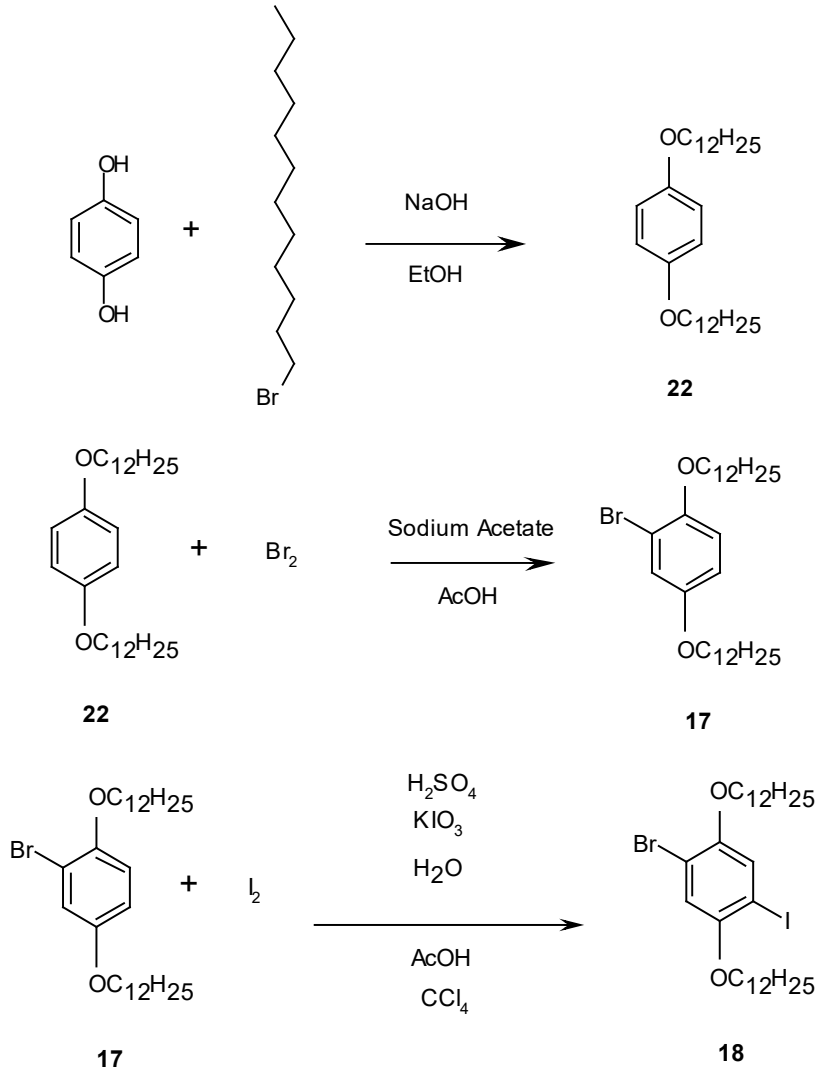
In Chapter 3.1.4, two polymers having the same alkoxy side chains (ethyl hexyl groups) and different aliphatic chain lengths in the polymer backbone, were synthesized. The main target of the synthesis of these polymers was to study the effect of the aliphatic spacer length in the polymer backbone on the opto-electronic properties of the polymers.

It is interesting at this point to study the effect of the chain length of the alkoxy aliphatic side chains on the macromolecular arrangements of the polymer and, consequently, on the opto-electronic and physical properties of the polymers. For this purpose, Polymer **44** and Polymer **45** were synthesized having $C_{12}$-alkoxy side chains and a $C_2$-aliphatic spacer and a $C_3$-aliphatic spacer, respectively. The opto-electronic properties of these polymers should be compared to Polymers **15** and **36**.

### 3.2.1 Synthesis of Monomer 21

The synthesis of Monomer **21** was the first step in the preparation of Polymers **44** and **45**. The synthesis of **21** started with the conversion of hydroquinone to the dialkoxy $C_{12}$ molecule, compound **22,** using dodecyl bromide and potassium hydroxide (**Scheme 19**). This molecule was mono-brominated using bromine in acetic acid, in the presence of sodium acetate, to yield the $C_{12}$-dialkoxy mono-bromo benzene compound **17**. This compound was purified from the dibromo compound by repeated recrystallization from ethanol. The off-white crystalline compound was converted to 2-bromo-5-iodo-1,4-bis(dodecyl)oxybenzene, compound **18**, using elemental iodine, potassium iodide in acetic acid, and a catalytic amount of sulfuric acid. A few milliliters of carbon tetrachloride were added to the reaction to solubilize the iodine sublimed during the reflux. After 30h, the acetic acid was removed and the residue was extracted several times with methylene chloride and water. To remove the residual iodine from the product, the organic layer was washed with a concentrated sodium sulfite solution. After

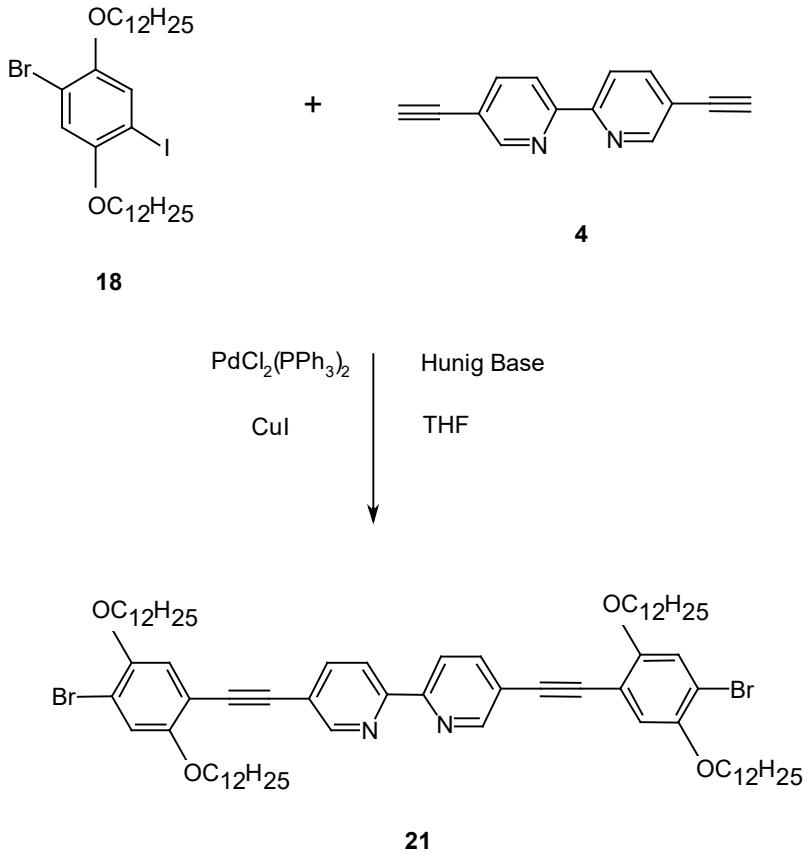
evaporation of the solvent, the final product was purified by recrystallization from methylene chloride:hexane (9:1) to yield a white crystalline solid.




**Scheme 19:** Synthesis of 2-bromo-5-iodo-1,4-bis(dodecyl)oxybenzene **18**

To arrive at monomer **21**, 5,5'-diethynyl-2,2-bipyridine **4** was reacted with 2-bromo-5-iodo-1,4-bis(dodecyl)oxybenzene **18** in a molar ratio of 1 to 2.2, using Sonogashira Pd-cross coupling reaction conditions (**Scheme 20)**. The reaction was carried out in freshly distilled toluene using 1.5 mol % $PdCl_2(PPh_3)_2$ and 1.5 mole % CuI. The reaction was carried out at 0 $^0$C for the first 3h and then at room temperature over night. Upon removal of the solvent, the reaction was worked-up with water/methylene chloride extractions.

The residue was then purified by column chromatography with hexane/ethyl acetate (9:10). The $^{1}$H-NMR of the molecule shows the quintet of the $CH_2$-protons adjacent to the oxygen atoms in the alkoxy side chains at $\delta$ = 4.01 ppm. In addition, the aromatic ring protons show two singlets at $\delta$ = 7.04 and $\delta$ = 7.13 ppm, while the protons of the bipyridine rings appear at $\delta$ = 7.92, 8.43, and 8.80 ppm. The structures of the molecules were further confirmed by $^{13}$C-NMR analysis and mass spectroscopy.

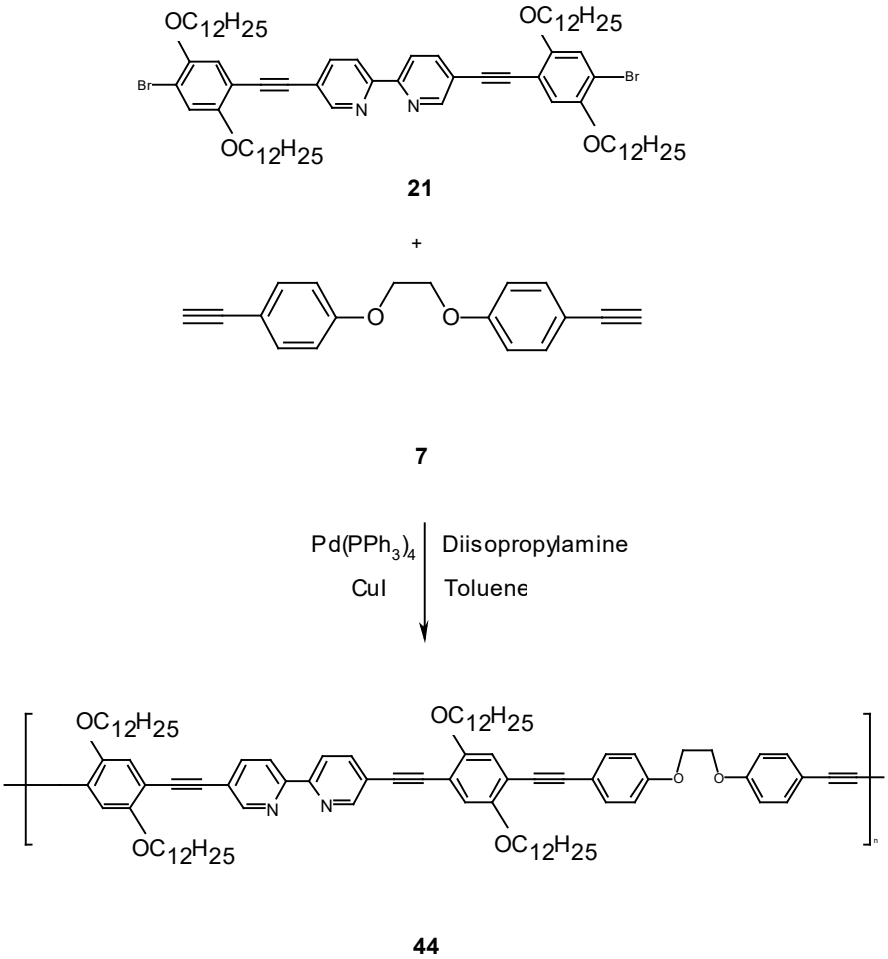



**Scheme 20:** Synthesis of Monomer **21**

### 3.2.2 Synthesis of the Alternating Copolymers 44 and 45

To synthesize polymer **44**, the di-bromo monomer **21** was reacted with 1,2-bis(4-ethynphenoxy)ethane 7 in a molar ratio of 1:1, according to Sonogashira Pd-cross coupling reaction conditions (**Scheme 21**). Both monomers were dissolved in freshly

dried toluene after exhaustive degassing with argon. Tetrakistriphenylphosphine palladium was used at 4 mol %. Using this catalyst instead of $PdCl_2(PPh_3)_2$ proved to be more efficient and leads to polymers with higher molecular weights. Copper iodide was selected as the cocatalyst and diisopropylamine as the base. After 68h, the reaction was stopped and the mixture was extracted several times with water in order to remove any salts formed as byproducts. The organic layer was dried and the solvent was evaporated. The organic residue was dissolved in methylene chloride and precipitated from cold methanol in order to remove low molecular weight oligomers and trace amounts of the starting monomers. The orange solid was filtered and washed several times with methanol. The solid was further purified by extraction with hot methanol in a Soxhlett apparatus for 72h. The resulting polymer was dried and further characterized.




**Scheme 21:** Synthesis of Polymer **44** from Monomer **21** and Monomer **7**

The synthesis of Polymer **45** involves the reaction of the dibromo monomer **21** with 1,3-bis(4-ethynphenoxy)propane **10**, according to Sonogashira Pd-cross coupling reaction conditions, in a molar ratio of 1:1 (**Scheme 22**). The conditions selected for the polymerization were similar to those used for the preparation of Polymer **44**. The polymer obtained was found to be completely soluble in common organic solvents such as methylene chloride, DMSO, DMF, and THF.

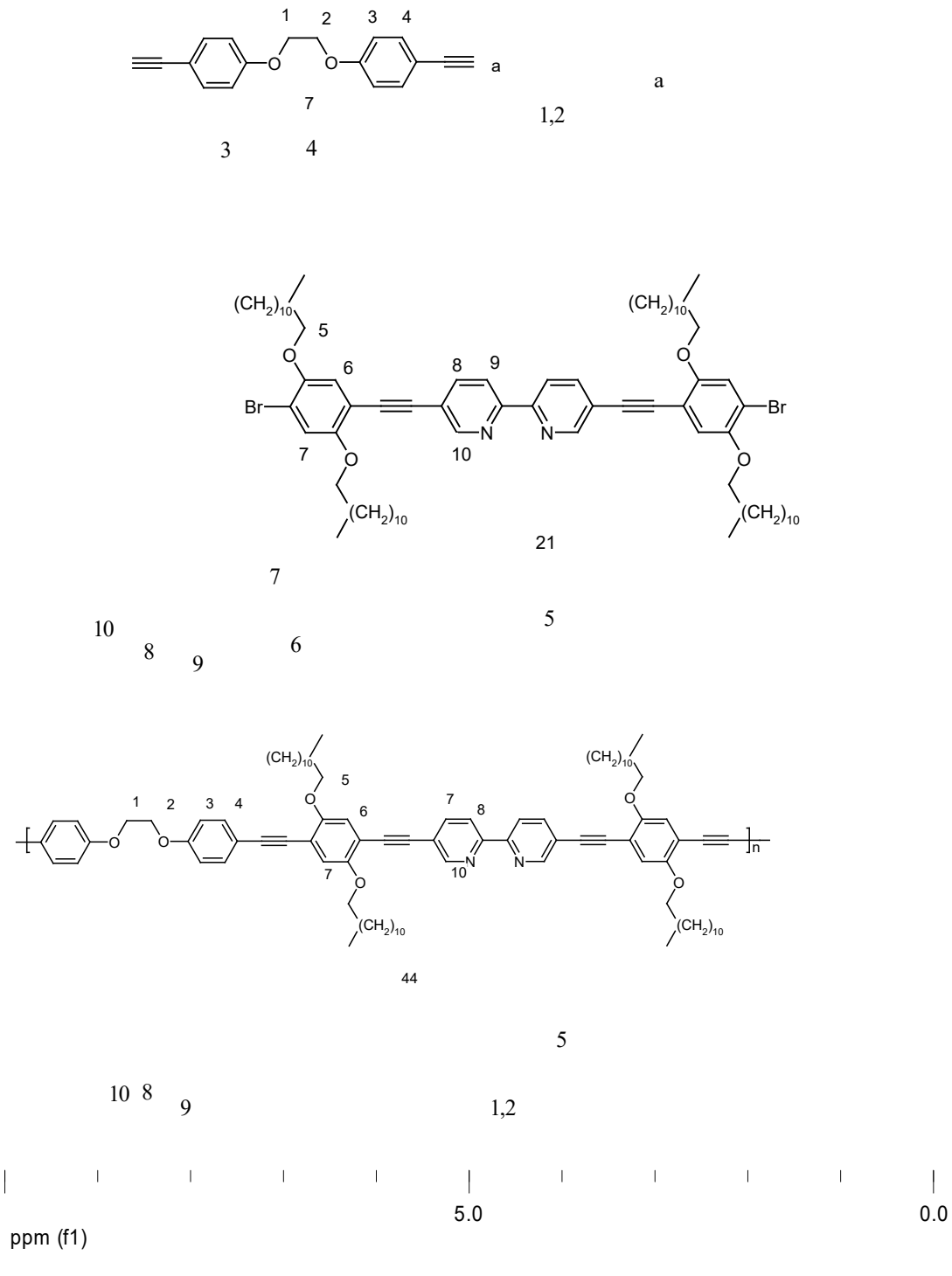
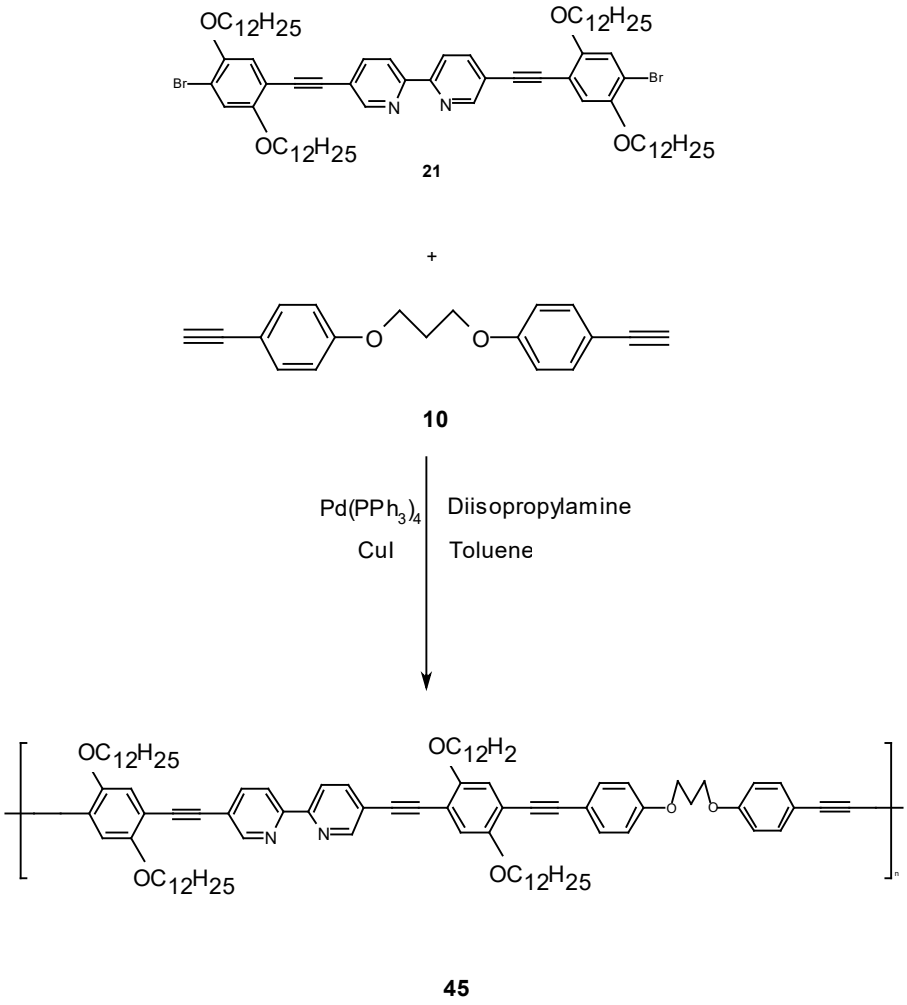



**Figure 6**: $^{1}$H-NMR of Polymer **44** Compared to Monomer **7** and **21**




**Scheme 22**: Synthesis of Polymer **45**

The $^{1}$H-NMR of Polymer **44**, compared to those of monomer **21** and monomer **7**, are illustrated in **Figure 6**. The spectra show the presence of the two ether $CH_2$-protons at $\delta$ = 4.31 and $\delta$ = 4.01 ppm. The first group belongs to the aliphatic spacer in the polymer backbone, and the second group at $\delta$ = 4.01 ppm is attributed to the alkoxy $C_{12}$ side chains ($OCH_2$). The integration ratio of these two groups was found to be 1:2, confirming the 1:1 ratio of the monomers in each polymer unit. The signals in the aromatic region could be accurately assigned to the aromatic and bipyridine rings in the polymer unit. The $^{13}$C-NMR spectra of the polymer compared to monomers **21** and **7** are illustrated in **Figure 6A**.

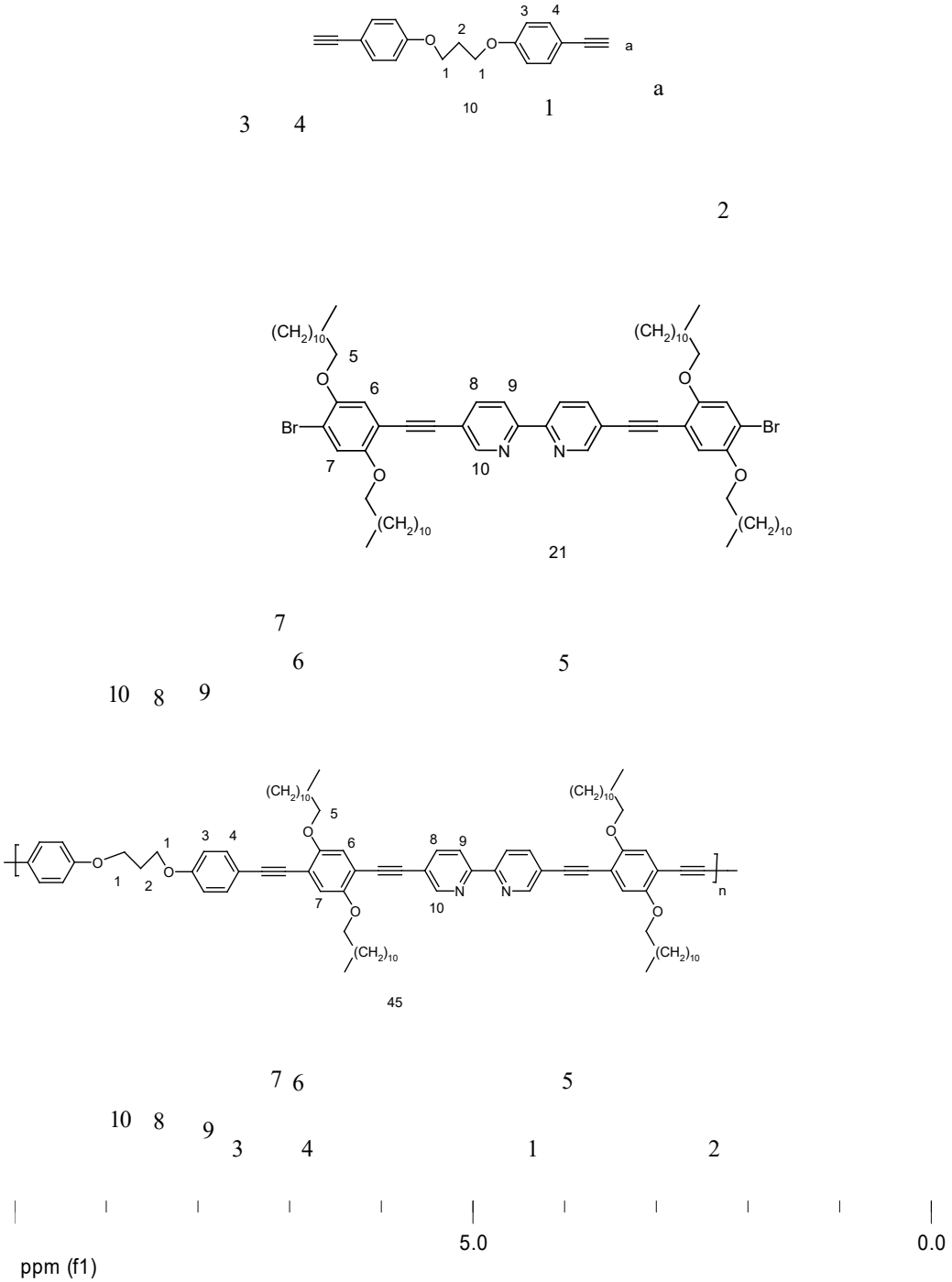



**Figure 7**: $^{1}$H-NMR of Polymer **45** Compared to Monomers **10** and **21**

The chemical shifts of the $CH_2$-ether protons of the backbone aliphatic spacer appear at $\delta$ = 69 ppm, with the ether side chain protons at $\delta$ = 70.1 ppm. The signals for the acetylene carbons were found in the expected range between $\delta$ = 80 and 96 ppm. The $^1H$ and $^{13}C$-NMR spectra of the polymer do not show any signals related to free acetylene groups, confirming the absence of alkene endgroups.

The $^1H$ and $^{13}C$-NMR spectra of Polymer **45** are illustrated in **Figure 7** and Figure **7A** (Appendix), respectively. Both spectra confirm the structure of the polymer. The integral ratio of the two ether groups of the polymer backbone and side chains at $\delta$ = 4.0 ppm and $\delta$ = 4.19 ppm is 1 to 2, as expected.

The molecular weights of the polymers were determined by gel permeation chromatography using polystyrene as the standard and THF as the eluent. The number average molar mass of Polymers **44** and **45** were found to be 7,099 and 7,268 g/mol, respectively. The polydispersity index was calculated and found to be 2.04 for Polymer **44** and 1.99 for Polymer **45**.

### 3.2.3 UV-Vis and Fluorescence Studies of Alternating Copolymers 44 and 45

We were very interested to investigate the effect of the length of the side chains on the opto-electronic properties of the final polymers. It is known in the literature that branching, and the length of the side chains in the polymers, could have an effect on the macromolecular arrangement of polymer segments and, consequently, on the physical and electronic properties of the polymers. For this reason, the UV-Vis and Fluorescence spectra of Polymers **44** and **45** with $C_{12}$-unbranched side chains were studied and compared to Polymers **15** and **36** with $C_6$-branched aliphatic side chains. The UV-Vis spectra of Polymers **44** and **45** were performed in methylene chloride and overlaid in **Figure 8**. As expected, the $\lambda_{max}$ undergoes a bathochromic shift compared to monomer **12** from 373 nm to 379 nm for Polymer **44** and 381 nm for Polymer **45**. This is due to the extended conjugation in the polymer backbone. It is interesting to note that the addition

of two aromatic rings and two alkyne units to the conjugated unit shifts the UV-maxima roughly 7-9 nm. This indicates that one can very precisely adjust the absorption maxima of the polymers according to the desired requirements. **Figure 8** shows that Polymer **45** with the $C_3$ aliphatic spacer in the backbone absorbs at slightly longer wavelengths compared to Polymer **44** with the $C_2$-aliphatic spacer. In addition, the maxima at lower wavelengths are well resolved and more pronounced in the former polymer. This could be attributed to the higher flexibility of the polymer chains with the $C_3$-spacer compared to the polymer with the $C_2$-spacer.

By comparing the absorption maxima of the polymers with ethylhexyl substituents (Polymers **15** and **36**) to the polymers with unbranched dodecyl substituents (Polymers **44** and **45**) one notices that the absorption maxima of Polymers **15** and **36** are bathochromic shifted. In addition, the difference in the shifts between the polymers with shorter aliphatic spacers in the backbone is larger than with the longer $C_3$ spacer.

The Fluorescence spectra in **Figure 8A** show that the emission maxima of Polymers **44** and **45** are similar at 469 nm, with a Stokes' shift of 79 nm. It seems that the length of the aliphatic spacer in the polymer backbone does not have any effect on the emission maxima of the fluorescence. However, the presence of branched aliphatic side chains on the polymer chain shift the fluorescence maxima bathochromically by 20 nm (**Figure 8A**) compared to the unbranched $C_{12}$ aliphatic side chains in Polymers **44** and **45**.

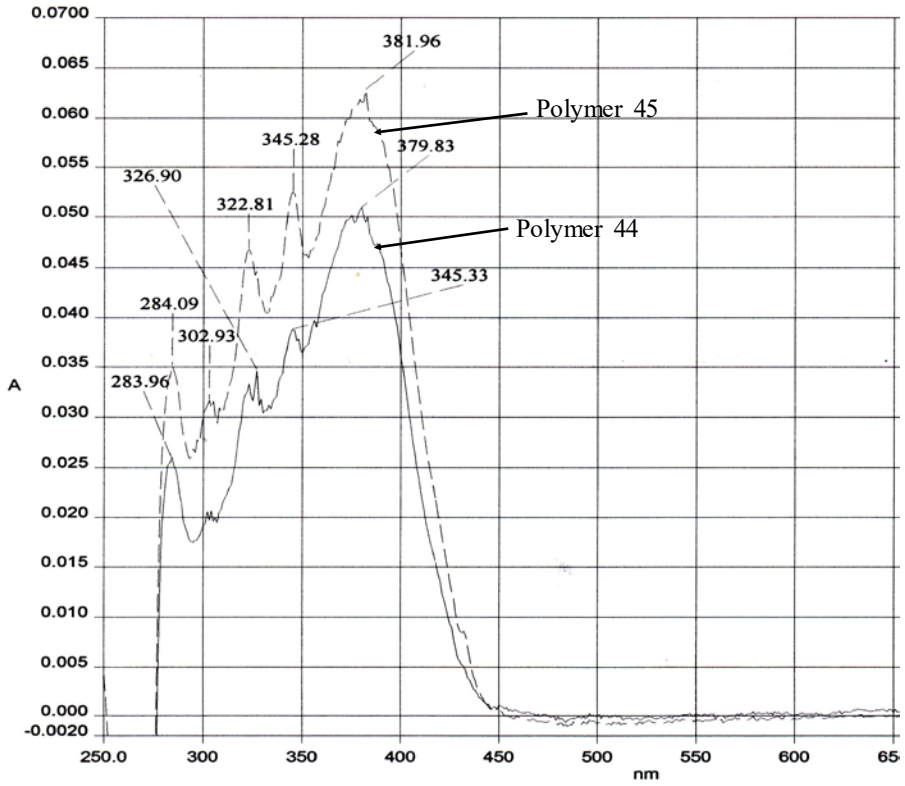



**Figure 8**: The UV-Vis of Polymers **44** and **45** in Methylene Chloride

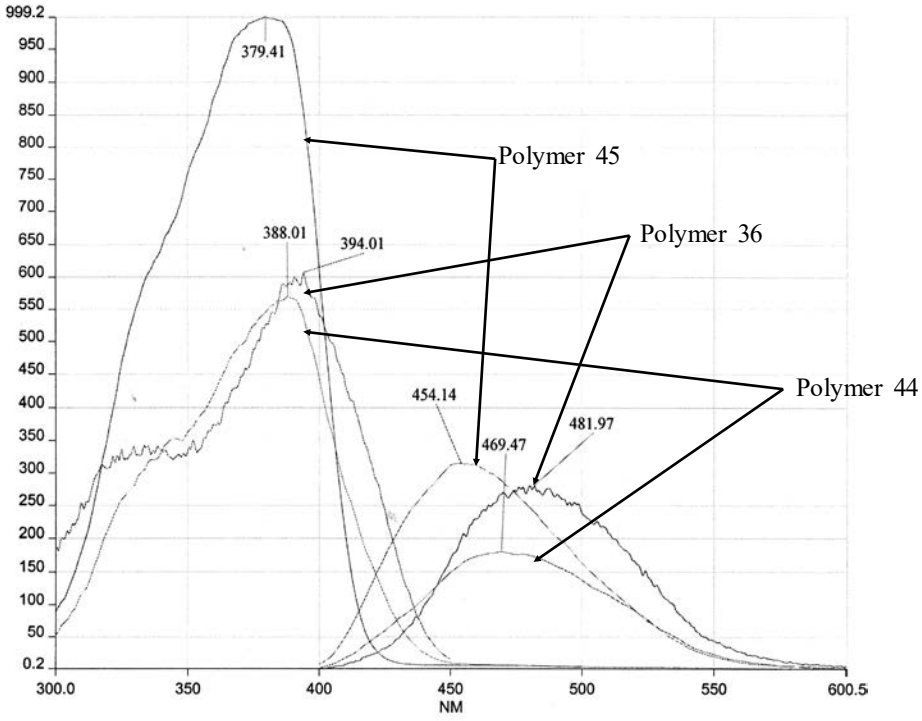
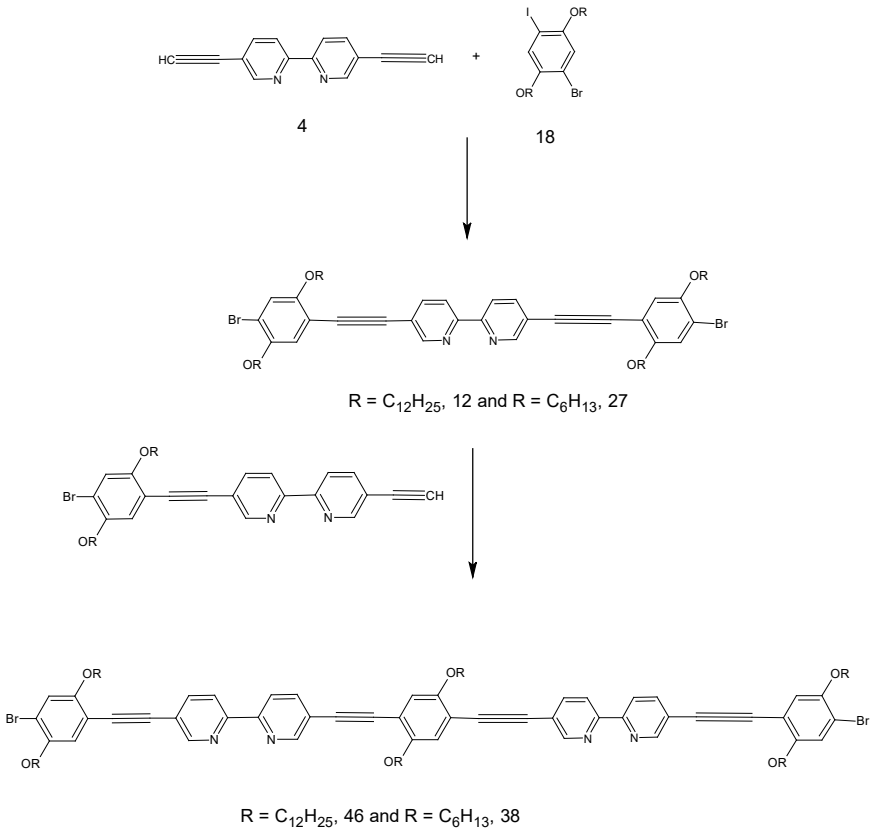



**Figure 8A**: The Excitation Emission Fluorescence Spectra Comparison of Polymers **36**, **44** & **45**

### 3.3 Polymer 39 and Polymer 47 with Extended Conjugated Units

#### 3.3.1 Synthesis of Monomers 46 and 38 with Two Bipyridine Units and Three Alkoxy-Substituted Aromatic Rings

During the synthesis of monomers **21** and **27** (**Scheme 20**), we observed on the TLC plates of the reaction the presence of other side products, with higher molecular weights than the desired molecule **21** or **27**. This new molecule was isolated in 40 % yield after column chromatography. To our surprise, the molecules isolated contain two bipyridine units and three alkoxy substituted aromatic rings. It appears that during the reaction, the bipyridine diacetylene **4** is reacting
with one iodo-bromo molecule **18,** forming a bromo-acetylene intermediate, which in turn




**Scheme 23**: Formation of Molecule **38** and **46** with Extended Conjugation

reacts with one mole of the dibromo compound **12** forming the large dibromo molecule **46** (**Scheme 23**). The $^{1}$H-NMR of this molecule (**Figure 11**) shows the presence of two different $OCH_2$-triplets at $\delta$ = 4.00 ppm and $\delta$ = 4.07 ppm. One of the $CH_2$-ether groups belongs to the aromatic ring between the bipyridine rings (center) and the other signal belongs to the $CH_2$-ether groups on the outer aromatic rings (ends). The integral ratio of the two groups was found to be 4 to 8.This indicates the presence of three aromatic rings in the molecule, two of which have similar chemical shifts. Furthermore, the aromatic rings show three different signals at $\delta$ = 7.039, 7.06, and 7.127 ppm. The two signals at 7.039 and 7.127 ppm belong to the external aromatic rings (ends) and the peak at $\delta$ = 7.06 ppm belongs to the aromatic ring in the middle of the chain (center). Taking into consideration the proton ratio of the bipyridine rings, the aromatic protons, and the $CH_2$-ether protons of the side chains, in addition to the $^{13}$C-NMR in appendix **Figure 11A,** it is evident that the new molecule formed is compound **46**. To support this finding, the MALDI-TOF mass spectrum was performed for this molecule. The MALDI-TOF spectrum in **Figure 9** shows the molecular peaks at 1899**.** The intensity of the isotopic ratio clearly confirms the presence of two bromine atoms in the molecule. The isotopic intensity distribution is very similar to the calculated one.

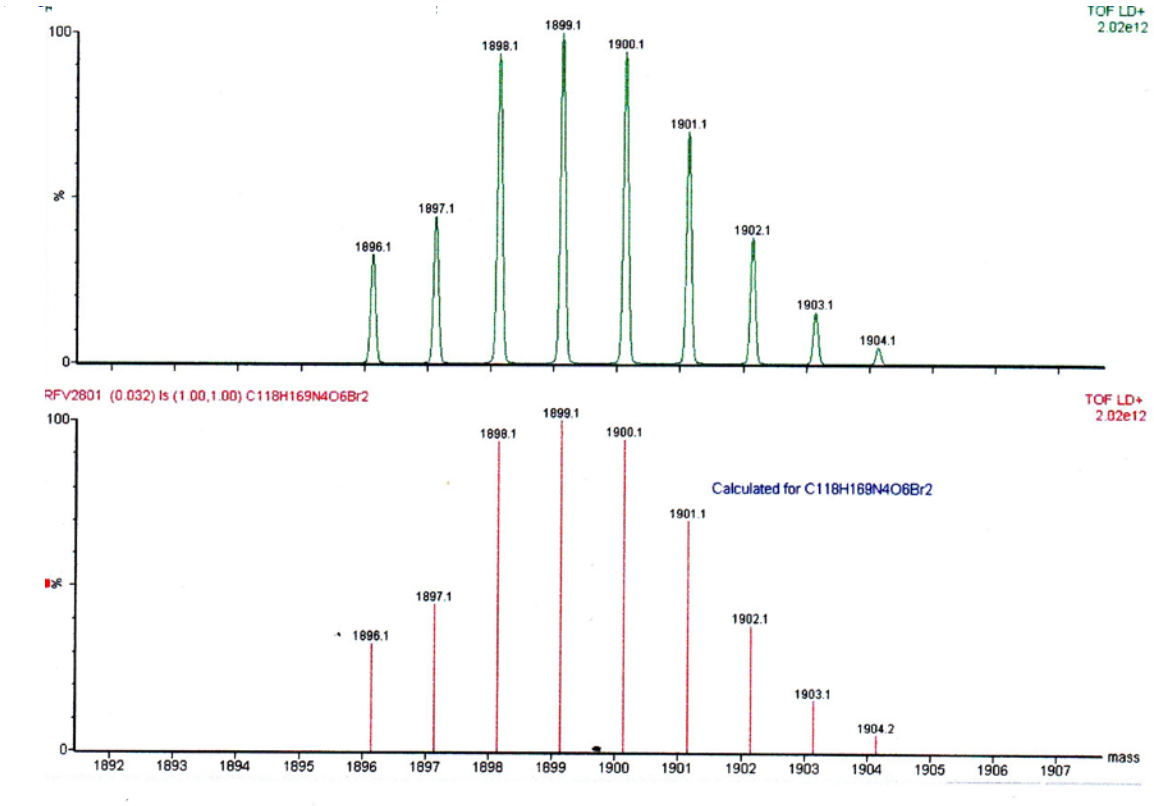



**Figure 9**: The Measured (top) and Calculated (bottom) MALDI-TOF spectrum of Monomer **46**

Similarly, during the synthesis of monomer **27**, the formation of a large molecule was observed. This molecule was isolated by column chromatography (45% yield) and analyzed using $^{1}$H-NMR, $^{13}$C-NMR, and MALDI-TOF mass spectrometry. The $^{1}$H-NMR in **Figure 12** shows the presence of two different signals for the $OCH_2$ groups in the alkoxy ether side chains. Three aromatic protons were observed at $\delta$ = 7.04, 7.07, and 7.12 ppm, which belong to the three aromatic rings in the extended conjugated unit. The integration ratio of the bipyridine protons to the aromatics and the alkyl chains confirm the structure of molecule **38**. To further confirm the formation of molecule **38**, MALDI-TOF mass spectrometry was performed. **Figure 10** shows the molecular peak of compound **38** at 1394**.** The isotopic distribution is very similar to the calculated values.

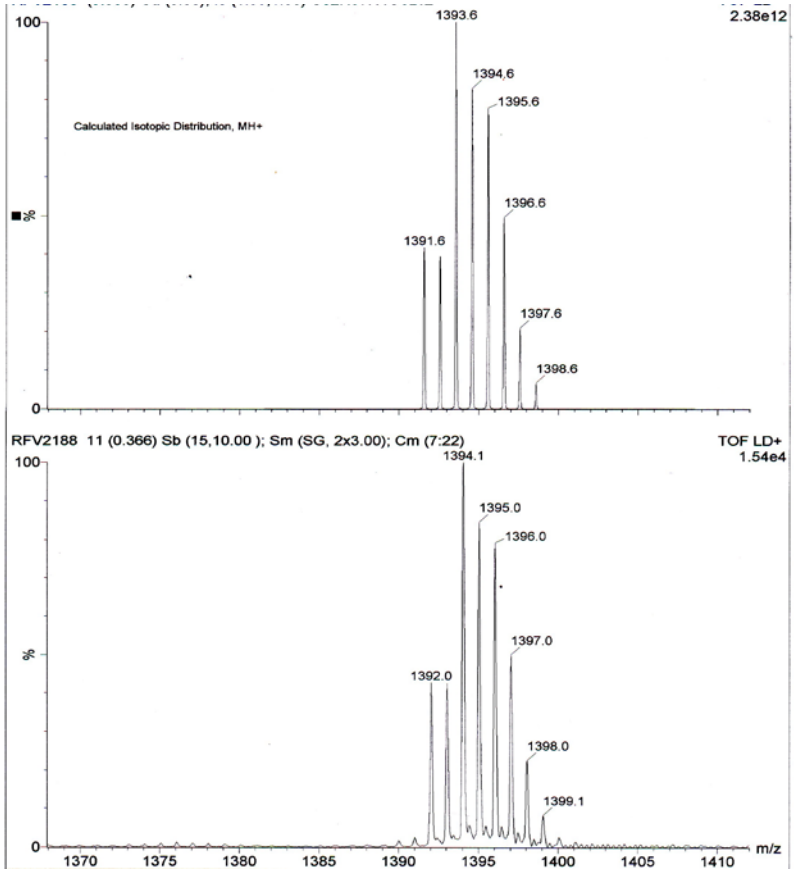
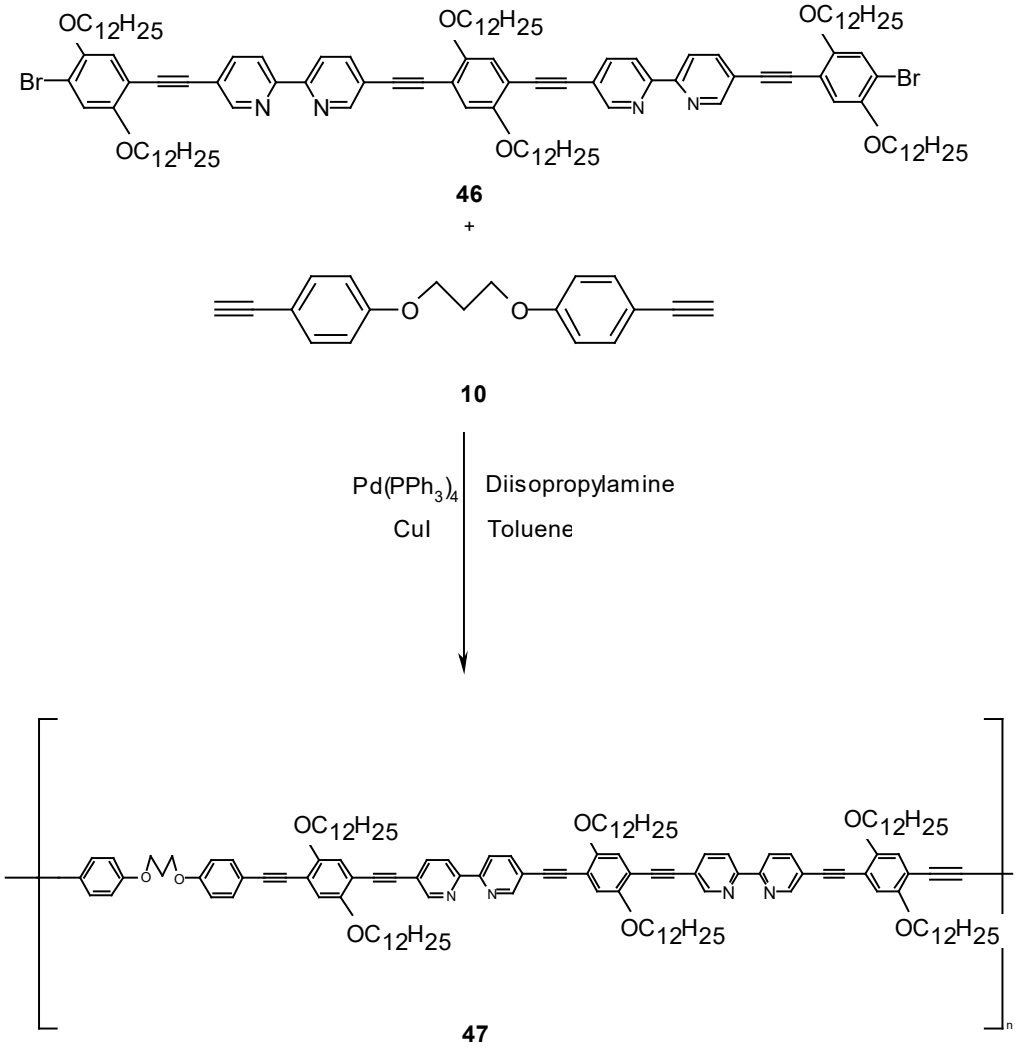



**Figure 10**: The Calculated (top) and Measured (bottom) MALDI-TOF Mass Spectrum of Monomer **38**

### 3.3.2 The Polymerization Reaction of Monomer 46 with 1,3-Bis(4-ethynphenoxy)propane 10

Monomer **46** having extended conjugation was reacted with the diacetylene monomer **10** in a 1:1 ratio according to Sonogashira Pd-cross coupling reaction conditions. Tetrakistriphenyl phosphine palladium, CuI, and diisopropylamine were employed in dry, degassed toluene. The reaction was maintained for 72h at 70 $^{0}$C. The reaction mixture was cooled down and the solvent was evaporated to dryness. The residue was dissolved in methylene chloride and precipitated from cold methanol. The polymer was filtered and the orange solid was extracted with hot methanol in a Soxhlett apparatus.




**Scheme 24**: Synthesis of Polymer **47** from Monomers **10** and **46**

The $^{1}$H-NMR of the polymer (**Figure 11**) shows three signals for $OCH_2$ ether groups at $\delta$ = 4.16, 4.06 and 4.00 ppm, which are assigned to the different ether groups in the side chains and the ether groups of the aliphatic spacer in the polymer backbone. In addition, the integration ratio of the aromatics to the bipyridine protons confirms the polymer structure.

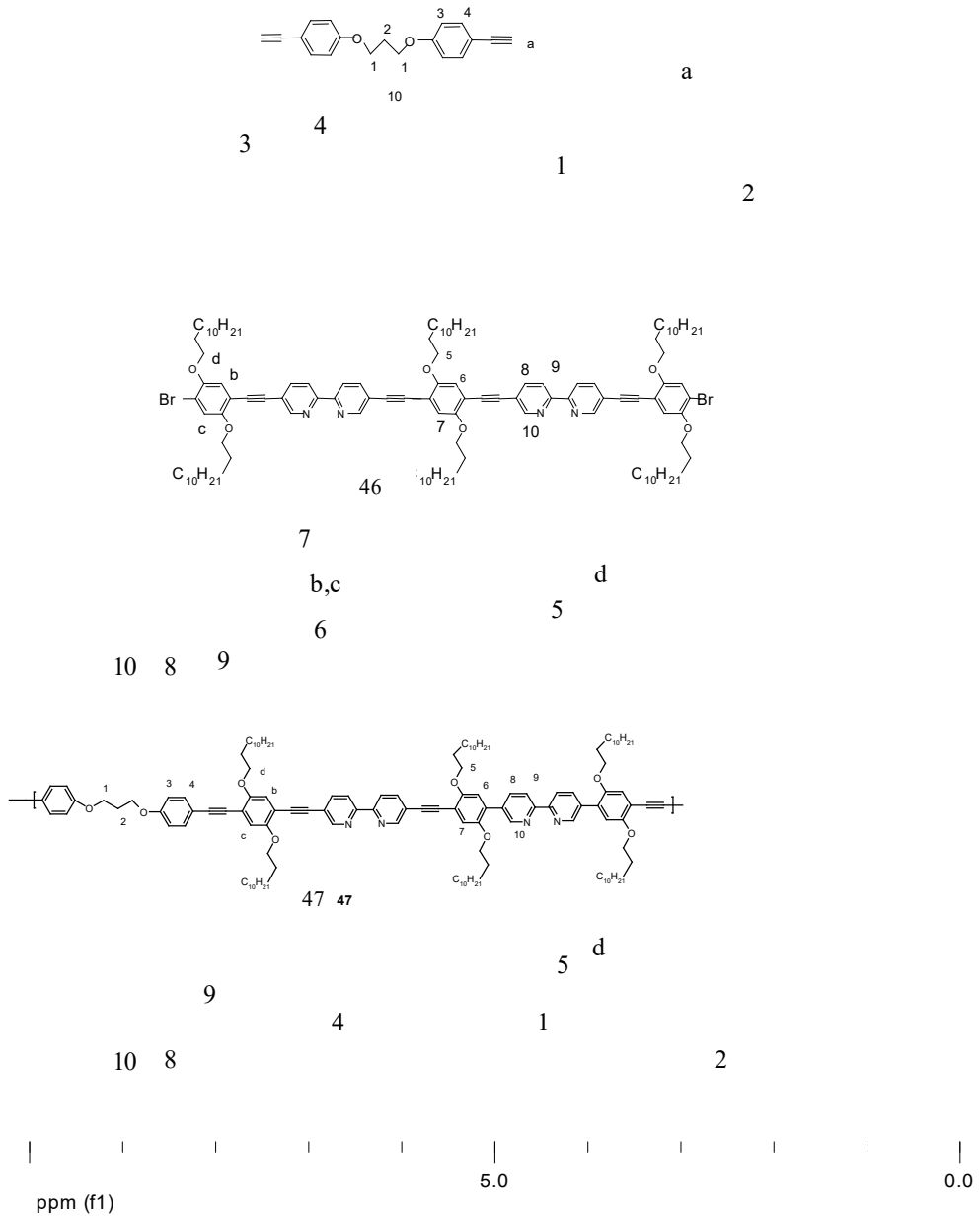
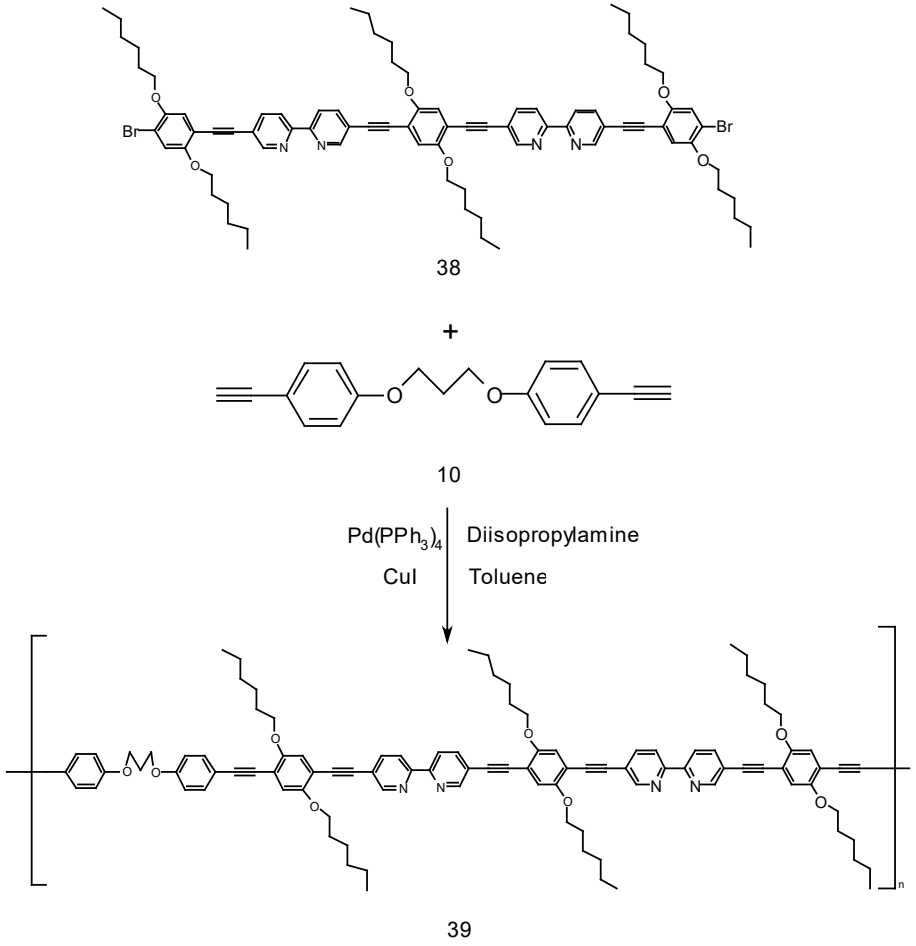



**Figure 11**: The $^{1}$H-NMR of Polymer **47** Compared to Monomer **46** and Monomer **10**

Using the same conditions as above, the polymerization of the dibromo compound **38** and the diacetylene compound **10** was carried out. The polymer work-up and purification was performed in the same manner as for polymer **47**.




**Scheme 25**: Synthesis of Polymer **39** from Monomer **38** and Monomer **10**

The molecular weights of the polymers were determined by GPC using polystyrene as the reference. The number average molar weights were found to be 9,983 g/mol and 6,470 g/mol for polymers **39** and **47**, respectively. The polydispersity index for polymer **47** was found to be 1.67.

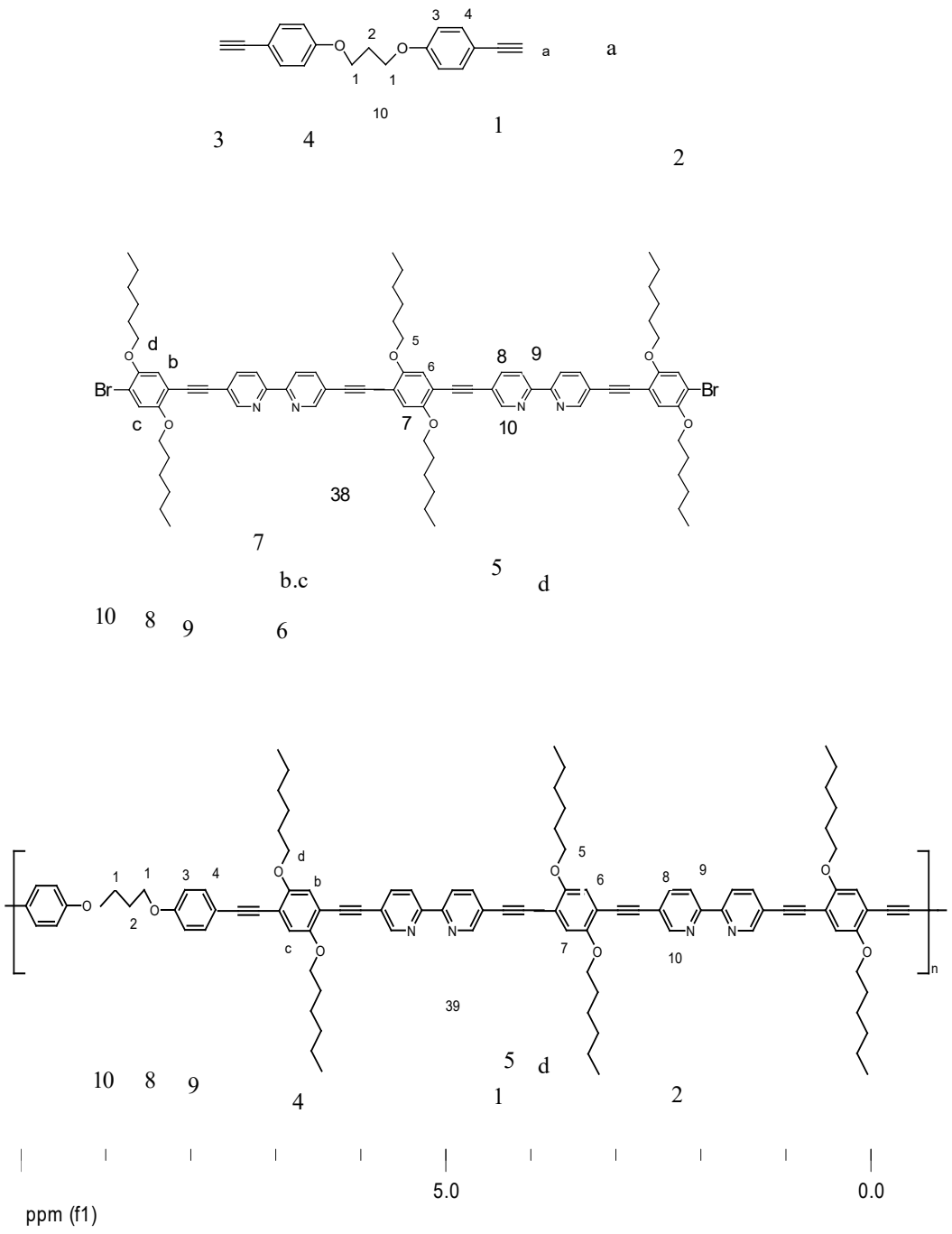



**Figure 12**: $^{1}$H-NMR Spectra of Polymer **39** Compared to Monomers **38** and **10**

### 3.3.3 Opto-electronic Properties of Polymers 39 and 47

It was of great interest for us to investigate the opto-electronic properties of the polymers with extended conjugation between the non-conjugated spacers. For this reason, polymers **39** and **47** were synthesized. Such polymers have one additional bipyridine unit and one additional aromatic unit than the previously synthesized polymers **15**, **36**, **44** and **45**. The UV-Vis spectra of both polymers **39** and **47** are illustrated in **Figures 13** and **14**. The absorption maxima of this extended polymer is bathochromically shifted (403 nm for **39** and 397 nm for **47**) compared to the other polymers with shorter conjugation (polymer **44** at 380 nm and polymer **45** at 382 nm).

The same trend of the shifts in the maxima was observed in the fluorescence spectra. The emission maxima of the polymers with extended conjugations were found to be bathochromically shifted.

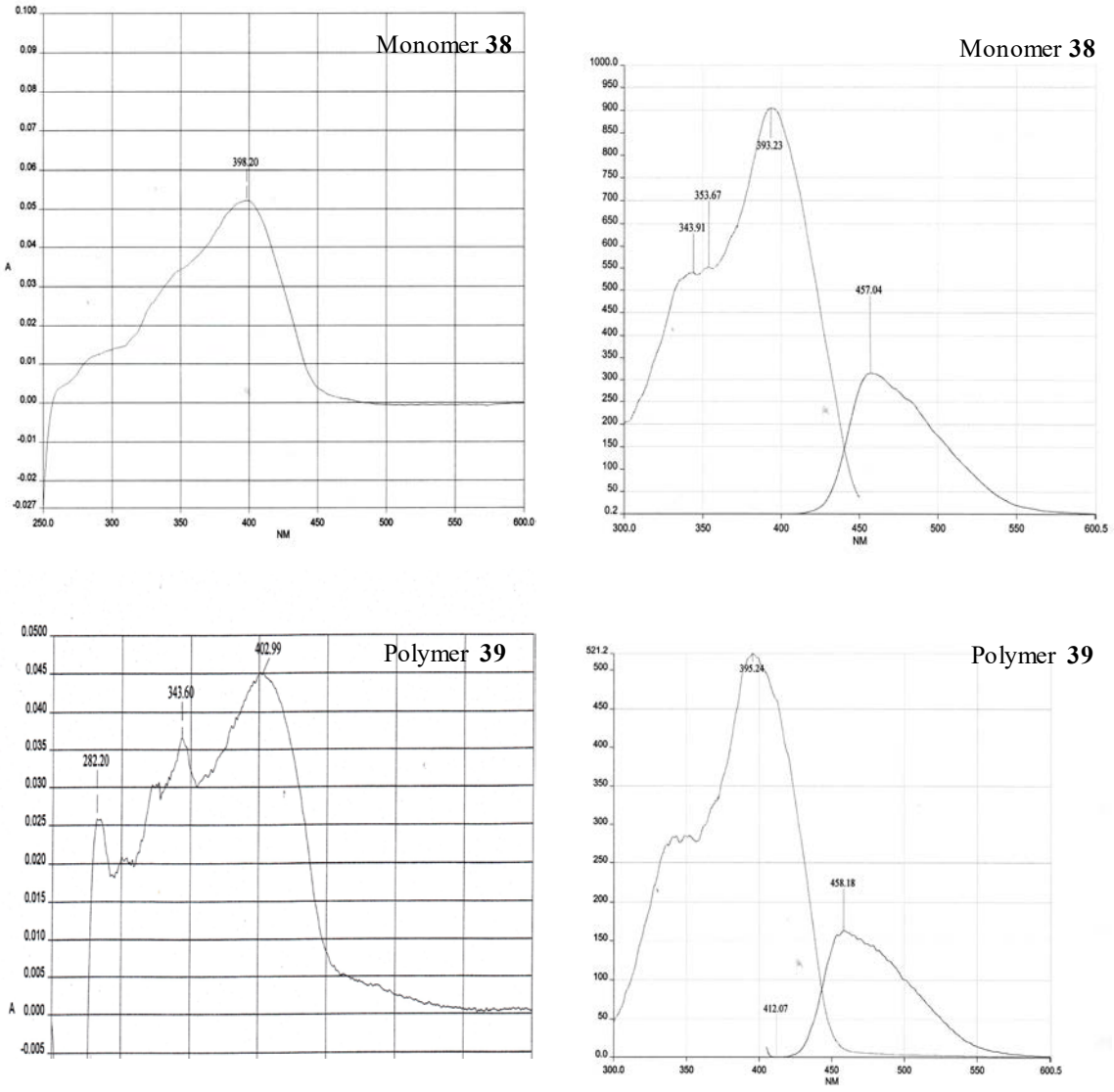



**Figure 13**: The UV-Vis and Fluorescence Spectra of Polymer **39** Compared to Monomer **38**

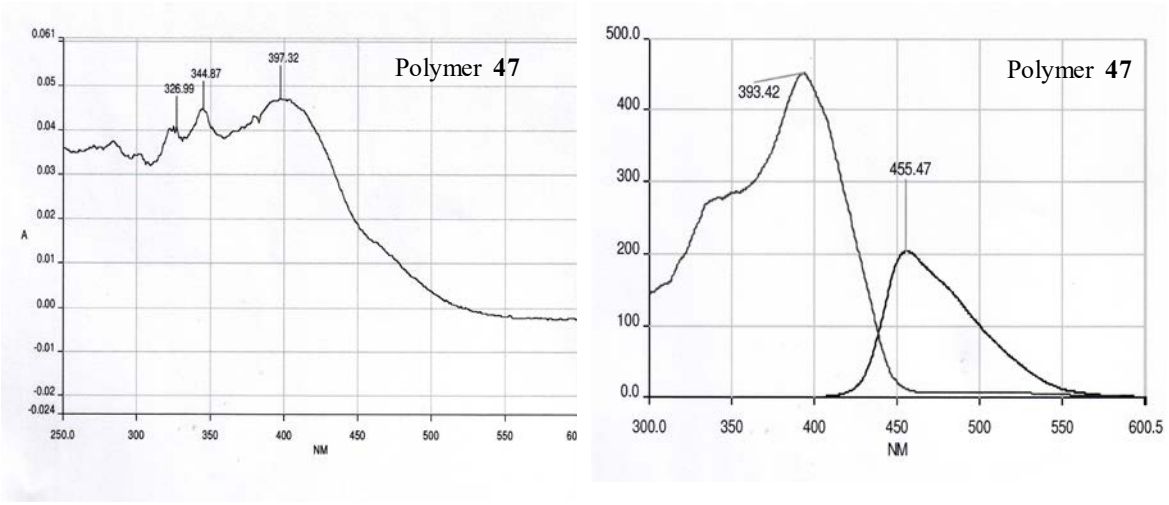


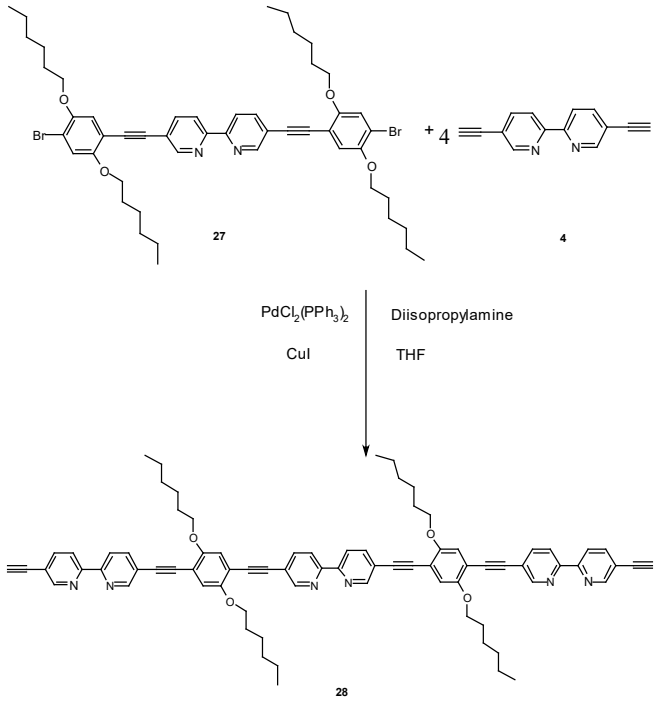

**Figure 14**: The UV-Vis and Fluorescence Spectra of Polymer **47**

## 3.4 Polymer 35 and Polymer 35-B With Three Bipyridine and Two Aromatic Units in the Conjugated Moiety

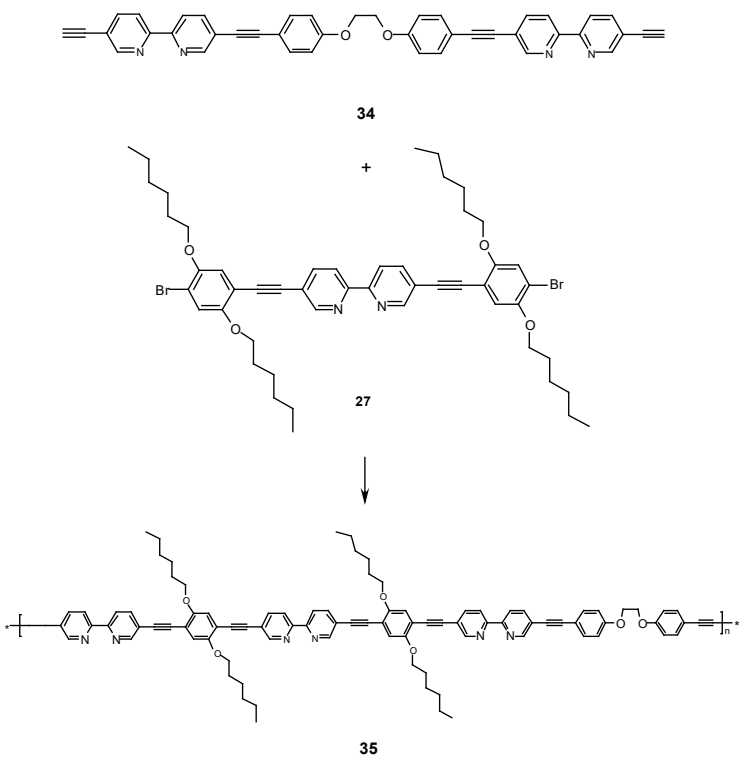
Since this work involves the synthesis of alternating copolymers with tailored opto-electronic properties, it was decided to synthesize polymers containing three bipyridine rings and two aromatic rings in the conjugated part. This new design should give the polymer completely different optical properties compared to the previously obtained polymers. Changing the extent of the conjugation will shift the UV and fluorescence to new maxima in a very measured way, allowing for the production of new polymers for specific applications.

### 3.4.1 Synthesis of Polymers 35 and 35-B

The first approach taken to synthesize polymer **35** was to prepare the diacetylene compound **28** (scheme **26**) and to further react it with the dibromo compound **5**, in order to arrive at polymer **35.** To synthesize monomer **28** the dibromo compound **27** was reacted with 2.2 equivalents of bipyridine diacetylene **4** using $PdCl_2(PPh_3)_2$ and CuI. Freshly dried and distilled THF was used as the solvent of choice. The reaction started at 0 $^0$C for 3h and then for 24h at room temperature. At this time, the TLC showed complete conversion of the starting materials. However, the TLC also showed the formation of a mixture of oligomers. The target compound **28** was isolated in very low yield (10%) after multiple attempts at column chromatography. The ratio of the bipyridine diacetylene **4** to the dibromo-compound **27** was increased to 4-fold and in another experiment to 8-fold excess in hopes of suppressing the formation of the side products. These attempts all led to a mixture of products. An alternative approach to the target molecule was needed.

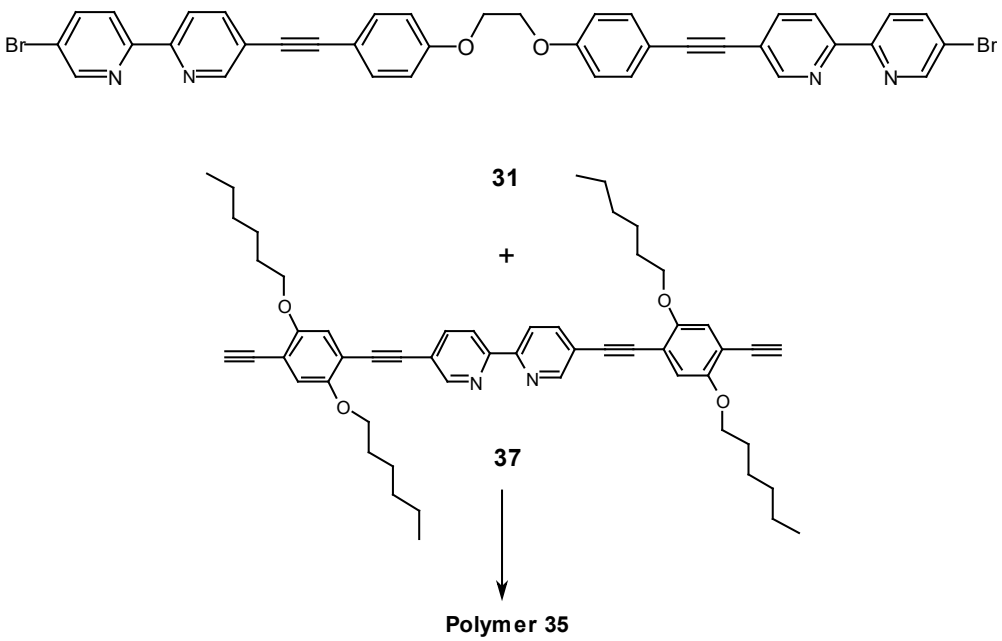



**Scheme 26:** Attempted Synthesis of the Diacetylene Compound **28**



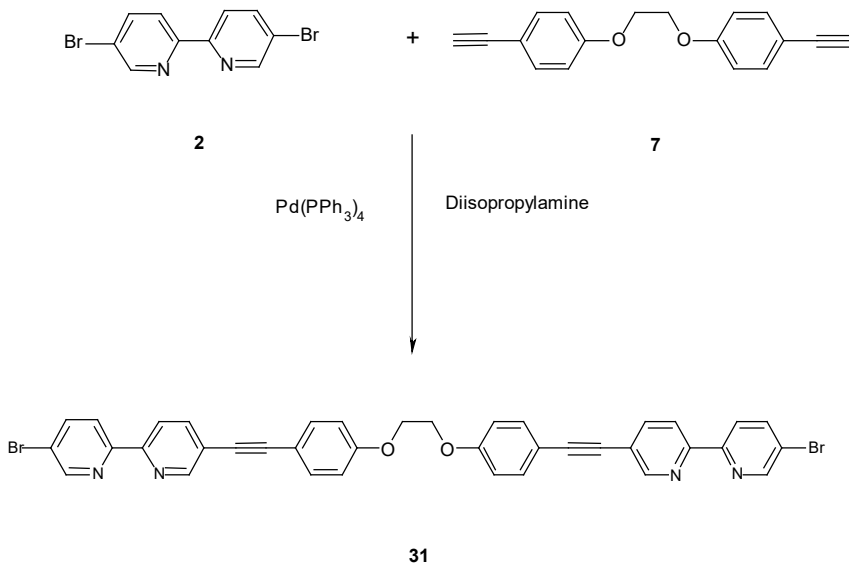

**Scheme 27:** Second Attempt to Synthesize Polymer **35**

The new strategy to arrive at polymer **35** was to prepare the dibromo monomer **31** and the diacetylene monomer **37** separately and further convert them to the target polymer according to Scheme **28**.




**Scheme 28**: Third Attempt to Synthesize Polymer 35

To prepare the dibromo monomer **31**, the diacetylene compound **7** was reacted with dibromobipyridine **2** in the molar ratio of 1 to 2.2 (**Scheme 29**). The catalyst used for this reaction was $Pd(PPh_3)_4$ in the presence of CuI and diisopropylamine. After 90h heating at 75 $^0$C, both starting materials disappeared from the solution and the TLC showed the presence of mixtures. In addition, insoluble material was isolated from the mixture. Repeating this experiment with different ratios of starting materials and catalyst concentrations did not yield any positive results.




**Scheme 29:** Attempted Synthesis of Monomer **31**

From the above attempts it could be concluded that the reaction of one bifunctional molecule with another bifunctional molecule, at different molar ratios, leads to the production of oligomeric mixtures.

Despite the fact that such reaction strategies are used in the literature successfully, it seems that this strategy is not suitable for Sonogashira cross-coupling reactions. It is believed that the intermediates formed during the catalytic cycle prefer to propagate to form mixtures of oligomers under the selected reaction conditions. For this reason, a new strategy was taken to arrive at the target polymer **35**. It was decided to build the diacetylene monomer **34** using a stepwise approach, according to **Scheme 30**. At first the unsymmetrical molecule **32** was prepared from dibromobipyridine **2** and the 2-methyl-3-butyn-2-ol (MBI) in a molar ratio of 1 to 1. The reaction was carried out according to Sonogashira Pd cross-coupling reactions at 55 $^0$C. After 24h, the reaction was stopped and the desired compound was isolated in 35 % yield using column chromatography. The unsymmetrical molecule **32** was reacted with the diacetylene compound **7** in a molar ratio of 2.2 to 1 using the same reaction conditions as for the preparation of molecule **32**.

As the reaction proceeded, the formation of a bright yellow solid was observed. The quantity of this solid increased with time. After 3 days, the TLC showed complete conversion of the starting materials. The reaction was stopped and the bright yellow solid was filtered and washed many times with methylene chloride. This solid was found to have poor solubility in all organic solvents such as chloroform, DMSO, DMF, and alcohols. The MALDI-TOF mass spectrum of this molecule confirmed the structure of the compound. **Figure 15** shows the MALDI spectrum after subtracting the matrix. The molecular mass of this molecule was confirmed. Despite the solubility problems in organic solvents, its deprotection to the diacetylene compound **34** was attempted. Two different approaches were tried. The first involved heating the protected molecule at 80 $^{0}$C in isopropyl alcohol with excess sodium hydroxide. The second approach employed heating the protected molecule in toluene at 130 $^{0}$C in the presence of sodium hydroxide pellets. In both cases, the suspended solid turned black without becoming soluble at any point. Further analysis of the black solid did not confirm the presence of the desired deprotected compound.

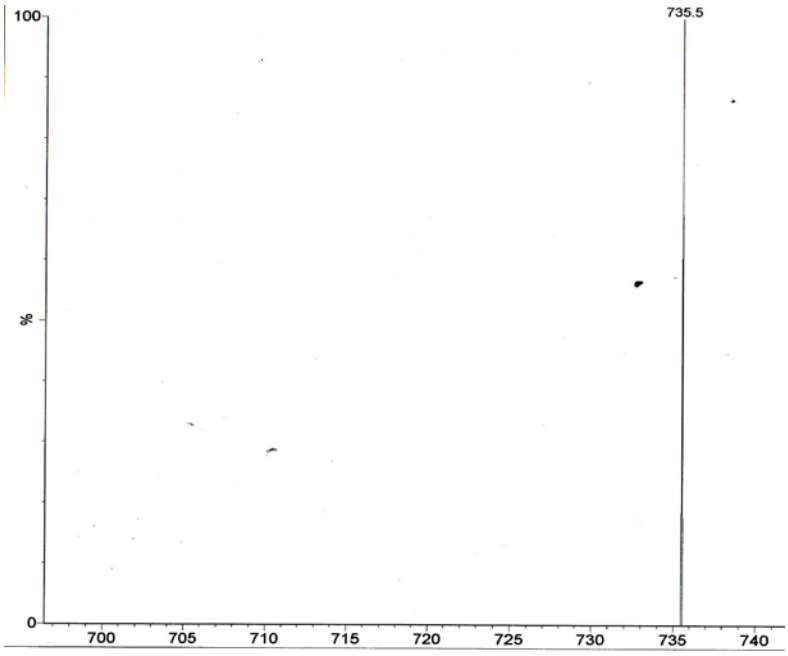
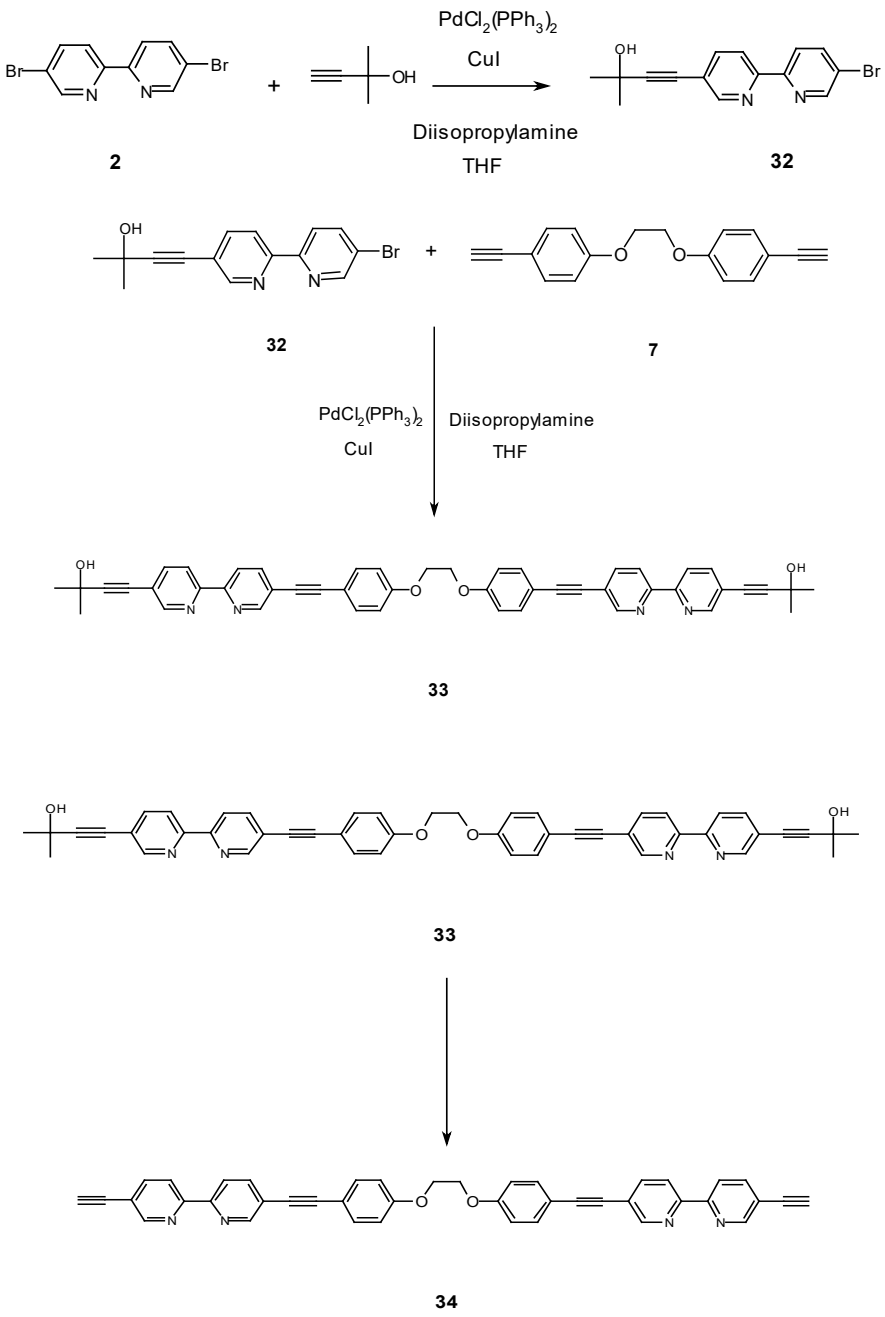


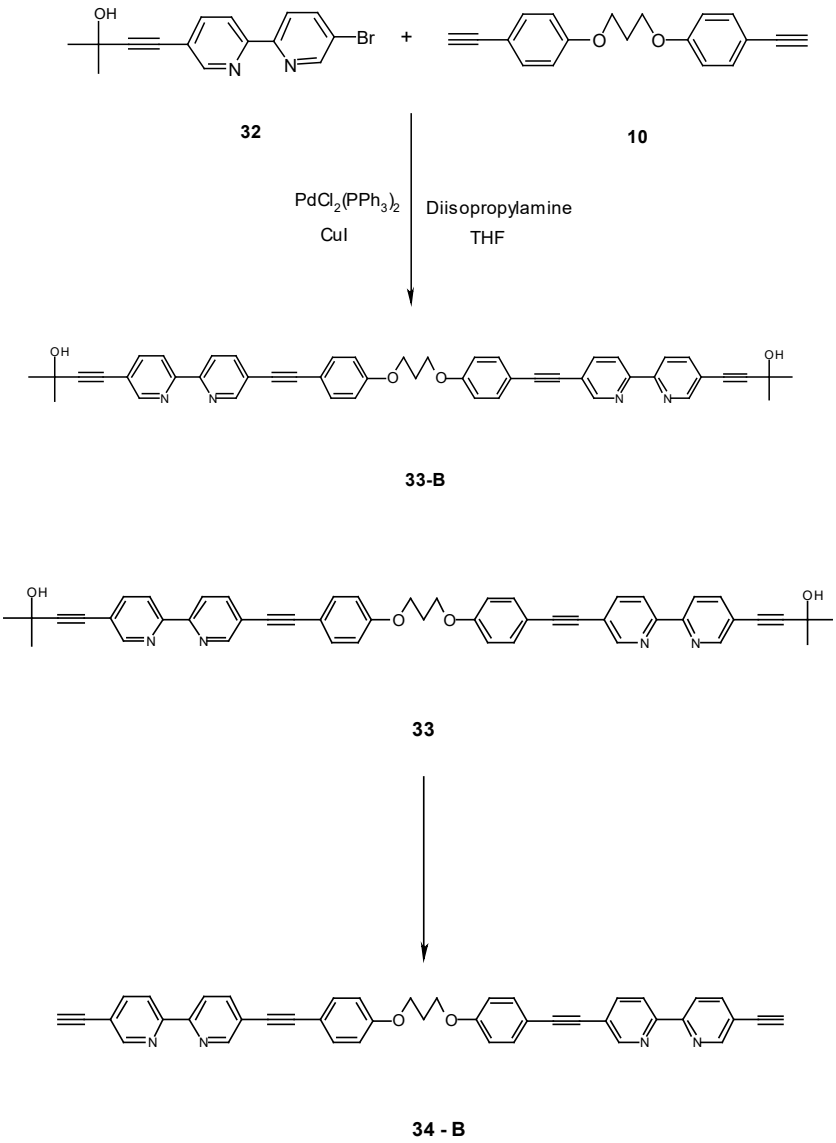

**Figure 15**: The MALDI-TOF Mass Spectrum of Compound **32**




**Scheme 30:** The Stepwise Synthesis of the Diacetylene Monomer **34**

To overcome the solubility problem associated with the protected intermediate **33**, a new molecule with a longer aliphatic $C_3$ spacer was synthesized. The synthetic approach chosen to prepare molecule **33-B** was similar to that used to prepare intermediate **33**. The resulting di-alcohol **33-B** was found to be soluble in common organic solvents such as methylene chloride, DMF, and DMSO. The deprotection of this

molecule was carried out in dry toluene in the presence of excess sodium hydroxide. After 3 days, the diacetylene monomer **34-B** was isolated in 44% yield.




**Scheme 31:** Synthesis of Key Molecule 34-B

The MADLI-TOF mass spectrum of molecule **34-B** (**Figure 16**) showed the formation of the diacetylene compound **34** after the deprotection step. The $^1$H-NMR spectrum in **Figure 17** shows the presence of the dialkoxy $CH_2$ –groups at 4.1 ppm and the acetylene protons at 3.3 ppm.

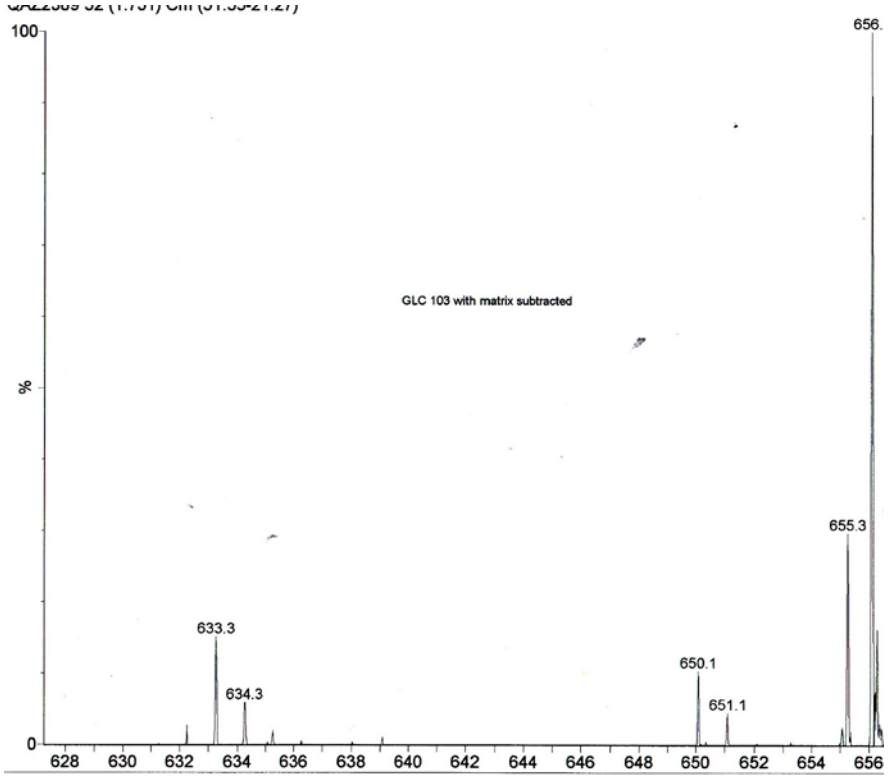



**Figure 16**: The MALDI-TOF Mass Spectrum of the Diacetylene Compound **34-B**

### 3.4.2 Synthesis of Polymer 35-B

After successfully preparing the diacetylene monomer **34-B**, this molecule was reacted with the dibromo compound **27** in a molar ratio of 1 to 1, to yield the target polymer **35-B**. The reaction was carried out according to Sonogashira Pd-cross coupling reaction conditions, in dry toluene and in the presence of CuI and diisopropylamine. The reaction mixture was stirred at 70 $^{0}$C for 3 days. The reaction mixture was cooled to room temperature and extracted three times with water. After removing the solvent, the solid residue was dissolved in concentrated methylene chloride and precipitated from cold methanol in order to remove low molecular weight compounds. The solid was further purified by extraction with hot methanol using a Soxhlett apparatus.

The $^1$H-NMR of the polymer shows the two $OCH_2$-ether protons of the aliphatic spacer in the polymer backbone and the $OCH_2$-ether protons of the aliphatic side chains. The integration ratio of these protons to each other and to the bipyridine rings clearly confirms the formation of the extended conjugated units of the target polymer **35-B**.

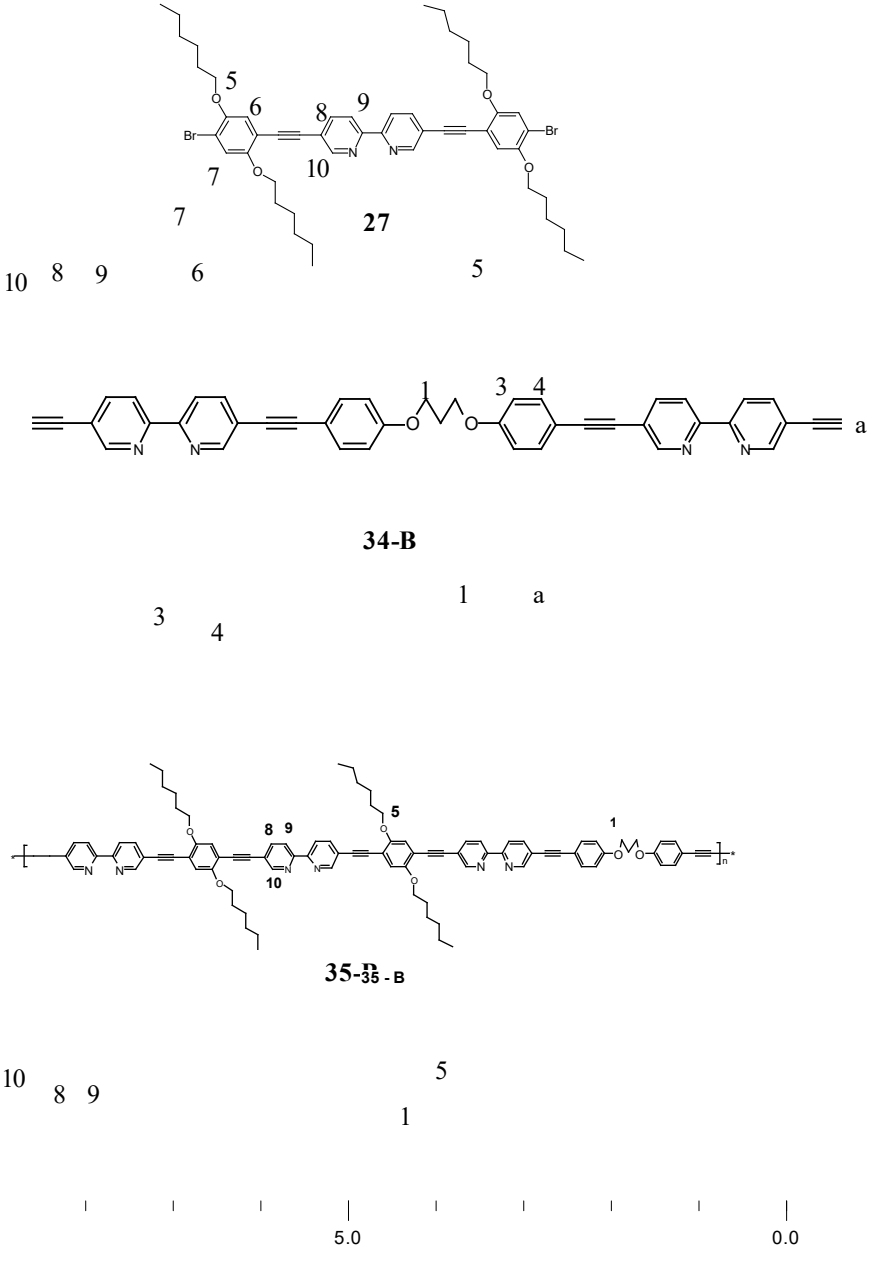



**Figure 17**: The $^1$H-NMR of polymer **35-B** compared to monomer **34-B** and **27**

The molecular weight of the polymer was determined using GPC techniques with THF as the eluent and polystyrene as the standard. The number average molecular weight

of this polymer was found to be 5,200 g/mol and its weight average molecular weight at 6,565 g/mol. The polydispersity index was found to be 1.34.

The opto-electronic properties of the polymer were studied using UV-Vis and fluorescence spectroscopy. The absorption maximum of the polymer was found at 381 nm. The fluorescence spectrum shows an emission maximum at 460 nm.

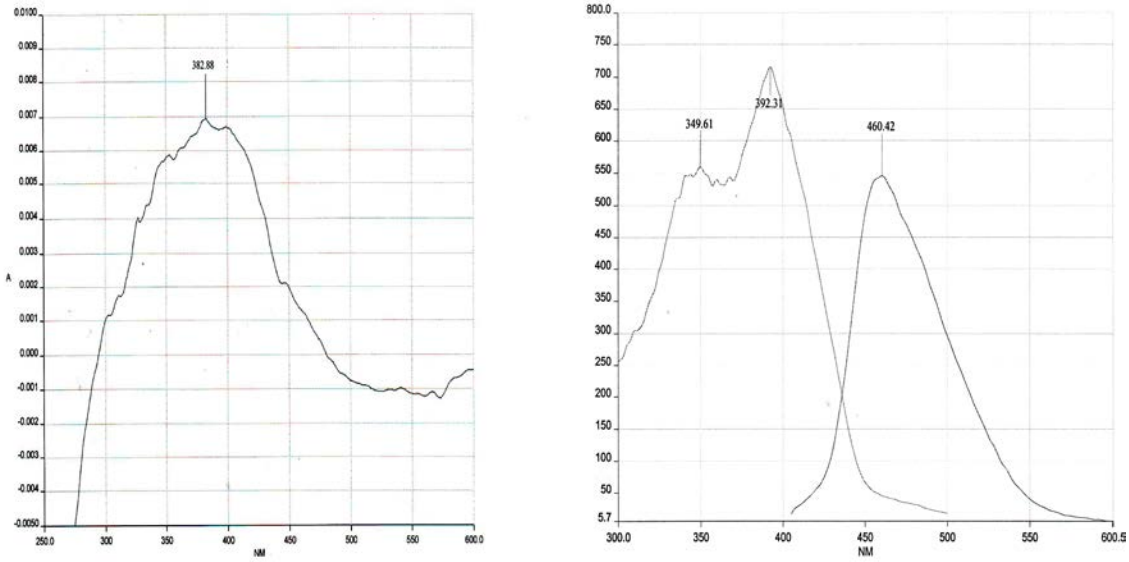



**Figure 18:** The UV-Vis and Fluorescence Spectra of Polymer **35-B**

# 4. Experimental Part

## 4.1 Experimental Techniques

**Melting Points:** All melting points were recorded on a Büchi Melting Point B-540 melting point apparatus.

**UV-Vis Spectroscopy:** All UV-Vis spectra were obtained on a Perkin-Elmer Lambda 12 Spectrometer. The maxima were recorded in nm, and the molar absorption coefficient ε is expressed in $1 \cdot mol^{-1} cm^{-1}$. The solvent used was methylene chloride (HPLC grade-Baker).

**Gel Permeation Chromatography (GPC):** GPC molecular weight determinations were made at a flow rate of 0.60 ml/min in THF on a Viscotek GPC max VE2001 system with a TDA203 triple detector array (including an RI detector). The UV detector is a Viscotek 2501. Two mixed bed Viscotek GPC columns were used with ViscogeI™ GMHHR-M and GMHHR-L columns (50-100,000 Å), and with polystyrene as standard.

**NMR-Spectroscopy:** Solution NMR spectra ($^1$H-NMR and $^{13}$C-NMR) were recorded on a Varian 200 MHz, Varian 400 MHz, Varian 500 MHz, or a Bruker 300 MHz instrument. All chemical shifts (δ) are recorded in parts per million. All spectra are referenced to TMS (trimethylsilylacetylene). Deuterated dichloromethane and chloroform were dried by sonication with $CaH_2$ and then deoxygenated with two freeze-thaw cycles under reduced pressure.

**Luminescence Spectroscopy:** All fluorescence spectra were recorded on a Perkin Elmer LS50B apparatus. Measurements were recorded in methylene chloride.

**Elemental Analysis (EA):** All C-H-N analyses were performed on a Perkin Elmer Series II Model 2400 instrument with Perkin Elmer AD-6 autobalance. Molar masses are expressed in g/mol.

**FT-IR Spectroscopy:** All IR spectra were recorded on a Perkin Elmer Spectrum 1000 instrument (KBr pellets). All peaks are expressed in $cm^{-1}$.

**Mass Spectrometry:** Mass spectra were obtained on Micromass MALDI micro MX and 70-250S instruments.

**Solvents:** Dimethyl sulfoxide was dried by fractional distillation under reduced pressure from $CaH_2$, followed by storage in air-free Chemglass storage flasks over 4A molecular sieves. Chloroform was dried by refluxing with $CaCl_2$ and stored in the dark, in air-free storage flasks over 4A molecular sieves. Dichloromethane was dried by refluxing with $P_2O_5$. $CH_2Cl_2$ was kept in air-free storage flasks in the dark. Tetrahydrofuran was pre-dried by stirring overnight with $CaH_2$ and then dried by refluxing with sodium/benzophenone until a dark blue colour was achieved. *N*-hexane was dried in the same manner as THF and stored in air-free storage flasks over 4A molecular sieves. Diisopropylamine was dried by distillation from NaH and then stored in air-free storage flasks in the dark. Triethylamine was dried over $CaSO_4$ followed by distillation from $CaH_2$ and stored in the dark. Toluene was dried with $CaH_2$ followed by further drying via fractional distillation from sodium. Pyridine was dried with NaOH, followed by fractional distillation. Anhydrous methanol was obtained by drying with $CaH_2$ followed by distillation.

**Chemicals:** Starting materials were all obtained from Sigma-Aldrich and Fluka and used without further purification. All air- and/or moisture-sensitive reactions were carried out under an inert atmosphere (Argon: 99.99 %, Air Liquide) using Schlenk techniques.

**Chromatography:** All column chromatography was conducted using *Fluka* brand silica gel 60 (70-230 mesh ASTM). All thin-layer chromatograms were run on *Merck* brand TLC aluminium sheets (Silica Gel 60 $F_{254}$).

### 4.1.1 Preparation of 2, 2'-Bipyridine salt – (1)

*a. Generation of HBr gas from Tetraline + Bromine*

Bromine was added dropwise from an addition funnel to a solution of tetraline and iron filings in a double-necked 1L round bottom flask. The resulting gas was forced through a washing bottle containing additional tetraline, then through a bubbler (cooled with dry ice). The HBr gas was then forced through teflon tubing to be used in the desired reaction. The process of HBr generation was maintained by the continuous slow addition of bromine. One must be very alert as there is frequently back-pressure occurring.

*b. Reaction of HBr with 2, 2'-Dipyridyl*

HBr gas was bubbled through a solution of 2,2'-Dipyridyl (1.9 g, 0.122 mol) in 200 ml of anhydrous methanol in a double-necked 1L round bottom flask. A dark yellow precipitate was observed dropping out of the orange solution. The bubbling was allowed to proceed for 1.5 hrs. The reaction was filtered and the desired salt was washed with two, 100 ml portions of hexane, collected and dried under vacuum to obtain a dark yellow solid.

| | |
|---|---|
| **Yield** | 22.80 g (60.0 %) |
| **m.p.** | 93 ºC |
| **$^{1}$H NMR** | (200 MHz, $D_2O$, 25 °C): δ = 7.85 ppm [dd, 2H, Ar-H], 8.42 ppm [dd, 4H, Ar-H], 8.78 ppm [dd, 2H, Ar-H] |
| **$^{13}$C {$^{1}$H} NMR** | (400 MHz, $D_2O$, 25 °C): δ = 122.82 ppm, 122.99 ppm, 141.93 ppm, 146.42 ppm |
| **EI-MS** | (70 eV): m/z (rel. int. %) 156 (100) $[M\text{-neutral}]^{+\bullet}$, 128 (30), 103 (5), 78 (25), 63 (3) |

### 4.1.2 Preparation of 5, 5'-Dibromo-2, 2'-bipyridine – (2)

The starting salt (**1**) (17.0 g, 0.054 mol) was placed into two stainless steel Teflon-lined Parr reaction bombs. To the bombs was added bromine and the mixtures were allowed to react at 190 °C for 80 hrs. The reactions were then allowed to cool for one day. When the bombs were opened, there was substantial release of HBr gas. The resulting orange solid was removed and ground into a fine pumpkin orange powder utililizing a mortar and pestle.

300 ml of a saturated sodium sulfate solution was prepared and the fine orange solid was added. After the immediate colour change from orange to pink, the solution was filtered and brought to pH 12 with a 3M NaOH solution, then extracted with four 100 ml portions of methylene chloride. This solution was allowed to stand overnight with sodium sulfate and filtered. The $CH_2Cl_2$ was then evaporated with a stream of nitrogen gas. The solid was then chromatographed (Hex/EA - 90:10) with the desired compound eluting first. The product is obtained as a colourless crystalline solid.

| | |
|---|---|
| **Yield** | 8.13 g (48 %) |
| **m.p.** | 223 ºC |
| **$^1$H NMR** | (400 MHz, $CDCl_3$, 25 °C): δ = 7.93 ppm [dd, 2H, Ar-H], 8.29 ppm [d, 2H, Ar-H], 8.70 ppm [d, 2H, Ar-H] |
| **$^{13}$C {$^1$H} NMR** | (400 MHz, $CDCl_3$, 25 °C): δ = 122.58 ppm, 139.96 ppm, 150.65 ppm |
| **EI-MS** | (70 eV): m/z (rel. int. %) 314 (100) $[M]^{+\bullet}$, 233 (23), 206 (30), 156 (14), 127 (8), 103 (8), 76 (20) |

### 4.1.2B Preparation of 5, 5'-Dibromo-2, 2'-bipyridine – (2) (Alternate)

In a 250 ml round bottom schlenk flask was added 2,5-dibromopyridine (5.07 g, 0.0213 mol) in 160 ml of dry toluene and allowed to degas for 45 minutes. Hexamethylditin (3.50 g, 0.0107 mol) was added to the solution followed by $Pd(PPh_3)_4$ (0.51 g, 0.0004 mol) and set to reflux for 4 d at 85 ºC. The solution was then cooled and diethyl ether (150 ml) was added. An off-white precipitate was filtered off and recrystallized from hexane to afford **2** as a white solid. (Yield: 1.3 g, 20 %)

### 4.1.3 Preparation of 5, 5'-Diethenyl(trimethylsilyl)-2, 2'-bipyridine – (3)

To a double-necked 1L round bottom flask equipped with two condensers was added 250 ml of ultra-dry THF (Na, benzophenone), dry diisopropylamine (32 ml) and 5, 5'-Dibromo-2, 2'-bipyridine (4.0 g, 12.7 mmol). This mixture was degassed with argon for 2 hrs. The following reagents were then added in sequence: trimethylsilylacetylene (6 ml, 4.96 g, 50.6 mmol), $PdCl_2(PPh_3)_2$ (0.8 g, 1.1 mmol, 10 mol %), CuI (0.45 g, 2.4 mmol). The reaction was stirred under argon until TLC analysis ($CH_2Cl_2$) showed complete conversion after 17 hrs. The flask was then subjected to additional warming for 2 hrs and the product was filtered through Celite. The THF was then removed by rotary evaporation and the desired solid was allowed to dry on the high vacuum pump for 2 hrs. Approximately 6.0 g of dark brown solid was then subjected to column chromatography (silica/ $CH_2Cl_2$) to obtain a colourless solid.

**Yield** 2.9 g (65 %)

**m.p.** 168 ºC

**$^1$H NMR** (500 MHz, $CDCl_3$, 25 °C): δ = 0.09 ppm [s, 18H, $C(C\underline{\mathbf{H}}_3)_3$], 7.86 ppm [dd, 2H, Ar-H], 8.36 ppm [d, 2H, Ar-H], 8.72 ppm [d, 2H, Ar-H]

**$^{13}C\{^1H\}$ NMR** (MHz, $CDCl_3$, 25 °C): δ = 95.87 ppm, 101.67 ppm, 120.72 ppm, 120.87 ppm, 140.17 ppm, 152.37 ppm, 154.47 ppm

**EI-MS** (70 eV): m/z (rel. int. %) 348 (73) $[M]^{+\bullet}$, 333 (100), 159 (30)

### 4.1.4 Preparation of 5, 5'-Diethynyl-2, 2'-bipyridine – (4)

In a 500 ml round bottom flask was added 5, 5'-diethynyl(trimethylsilyl)-2,2'-bipyridine(**3**) (2.60 g, 7.459 mmol) in 100 ml of MeOH and 100 ml of THF. The THF was absolutely necessary in order to solubilize the white solid TMS compound. To this mixture was added KF (0.93 g, 16.04 mmol) and the flask was covered with aluminium foil and allowed to stir overnight under an argon atmosphere. Upon completion of the reaction (TLC, Silica, $CH_2Cl_2$), the brown solution was filtered leaving a gold solid. This solid was suspended in 300 ml of $CH_2Cl_2$, filtered by gravity, and then subjected to rotary evaporation and several hours on the high vacuum pump. The resulting product was stored under argon in the dark in the fridge.

**Yield** 1.48 g (97 %)

**m.p.** Decomposition > 200 ºC

**$^1H$ NMR** (400 MHz, $CDCl_3$, 25 °C): δ = 3.31 ppm [s, 2H, C(C**H**)], 7.90 ppm [dd, 2H, Ar-H], 8.39 ppm [dd, 2H, Ar-H], 8.76 ppm [d, 2H, Ar-H]

**$^{13}C\{^1H\}$ NMR** (400 MHz, $CDCl_3$, 25 °C): δ = 80.89 ppm, 81.96 ppm, 119.77 ppm, 120.91 ppm

**EI-MS** (70 eV): m/z (rel. int. %) 204 (100) $[M]^{+\bullet}$, 177 (30), 102 (14), 75 (14)

### 4.1.5 Preparation of 1,2-Bis(4-bromophenoxy)ethane – (5)

NaOH pellets (12.4 g, 0.31 mol) were dissolved in 50 ml of $H_2O$ in a 250 ml round bottom flask. Solid 4-bromophenol (51.7 g, 0.30 mol) was added and the solution was allowed to stir for 30-40 minutes at 60-70 °C. The colour of the solution darkened from a light pink to deep rose. 1,2-dibromoethane (26.3 g, 12.06 ml, 0.14 mol) was added dropwise to the solution and the mixture was set to reflux at ~ 100-110 °C for ten hours. The reaction mixture was allowed to cool overnight.

The resulting off-white solid was then filtered and twice rinsed with 50 ml of distilled water to yield a pure white solid. The desired solid was then finely ground with a mortar and pestle and dried on a high vacuum pump. This was followed by recrystallization from hot ethanol. The resulting white crystalline solid was subjected to vacuum for 24 hrs, yielding a pure colourless crystalline solid product.

| | |
|---|---|
| **Yield** | 94.9 g (85 %) |
| **m.p.** | 147 ºC |
| **$^1$H NMR** | (200 MHz, $CDCl_3$, 25 °C): δ = 4.30 ppm [s, 4H, O-C**H**$_2$], 6.82 ppm [d, 4H, Ar-H], 7.39 ppm [d, 4H, Ar-H] |
| **$^{13}$C {$^1$H} NMR** | (400 MHz, $CDCl_3$, 25 °C): δ = 67.04 ppm, 113.76 ppm, 116.84 ppm, 132.68 ppm, 158.26 ppm |
| **EI-MS** | (70 eV): m/z (rel. int. %) 372 (100) $[M]^{+\bullet}$, 199 (70), 187 (8), 171 (30), 155 (48), 143 (30), 120 (86), 92 (43), 76 (37), 63 (38) |

### 4.1.6 Preparation of 4-(3-Methyl-3-hydroxy-1-butynyl)phenoxy ethane – (6)

In a dry, three-necked 250 ml round bottom flask, fitted with a condenser, argon inlet, and glass stopper, was placed a mixture of 1,2-bis(4-bromophenoxy)ethane (**5**) (4.0 g, 10.75 mmol) in dry triethylamine (160.0 ml). Gentle heating was required in order to solubilize the dibromo compound. The solution was degassed for 1 hr. 2-Methyl-3-butyn-2-ol (3.02 ml, 30.91 mmol) was then added and the reaction was heated to 80 °C. Triphenylphosphine (0.489 g, 1.864 mmol), Copper (I) iodide (0.1206 g, 0.633 mmol) and $PdCl_2[P(C_6H_5)_3]_2$ (0.1206 g, 0.172 mmol) were added to the reaction mixture producing a bright yellow coloured solution. The temperature was raised to 105 °C and maintained for 24 h, and then left to stir under argon for an additional 24 h at room temperature. The triethylamine hydrobromide salt was removed by filtration followed by washing with ether. The triethylamine and ether were removed under reduced pressure to leave a residual solid which was taken up in 100 ml of $CH_2Cl_2$ and washed with three 200 ml portions of 10 % sulfuric acid and with two 200 ml portions of distilled water. The organic layer was dried over $MgSO_4$, filtered, and concentrated to leave a crude product which was recrystallized from a mixture of $CH_2Cl_2$ and low boiling petroleum ether.

**Yield** 1.5 g (37 %)

**$^1$H NMR** (200 MHz, $CDCl_3$, 25 °C): δ = 1.61 ppm [s, 12 H, C**H**$_3$], 2.00 ppm [s, 2H, O**H**], 4.31 ppm [s, 4H, OC**H**$_2$], 6.87 ppm [d, 4H, Ar-H], 7.36 ppm [d, 4H, Ar-H]

**EI-MS** (70 eV): m/z (rel. int. %) 379 (65) $[M]^{+\bullet}$, 361 (10), 346 (100), 203 (14), 187 (20), 174 (33), 159 (44), 144 (25), 132 (112), 115 (30), 91 (17), 77 (10), 59 (15)

### 4.1.7 Preparation of 1,2-Bis(4-ethynphenoxy)ethane – (7)

In a 250 ml 2-neck round bottom flask fitted with a distilling head was placed 4-(3-Methyl-3-hydroxy-1-butynyl)phenoxy ethane (1.3 g, 3.43 mmol) in 85 ml of Toluene. The reaction mixture was made homogeneous by heating the solution to 70 °C at which time 35 ml of a 10 % NaOH/ MeOH solution was added. Toluene was distilled to half its original volume, at which point a sample was withdrawn and analyzed by TLC (silica: $CH_2Cl_2$). The reaction flask was replenished with toluene and the distillation/TLC/addition process was repeated three times. When the reaction was complete by TLC, toluene was removed under reduced pressure and the residual solid was purified by column chromatography (silica gel: $CH_2Cl_2$) to obtain a light tan solid.

| | |
|---|---|
| **Yield** | 0.65 g (73 %) |
| **m.p.** | 176 ºC |
| **$^1$H NMR** | (400 MHz, $CDCl_3$, 25 °C): δ = 2.95 ppm [s, 2H, C(C**H**)], 4.26 ppm [s, 4H, OC**H**$_2$], 6.83 ppm [d, 4H, Ar-H], 7.38 ppm [d, 4H, Ar-H] |
| **$^{13}$C {$^1$H} NMR** | (400 MHz, $CDCl_3$, 25 °C): δ = 66.77 ppm, 76.34 ppm, 83.85 ppm, 114.97 ppm, 115.07 ppm, 133.99 ppm, 159.24 ppm |
| **EI-MS** | (70 eV): m/z (rel. int. %) 262 (100) $[M]^{+\bullet}$, 145 (53), 118 (25), 101 (55), 89 (28), 75 (17), 63 (17) |
| **IR (cm$^{-1}$)** | 537.96, 635.76, 675.44, 830.53, 837.68, 935.64, 943.57, 1070.03, 1110.14, 1179.06, 1234.01, 1245.81, 1289.68, 1375.79, 1449.63, 1505.83, 1568.02, 1603.93, 2102.49, 2929.08, 3276.60 |

### 4.1.8 Preparation of 1,3-Bis(4-bromophenoxy)propane – (8)

NaOH pellets (6.21 g, 0.16 mol) were dissolved in 25 ml of $H_2O$ in a 250 ml double-necked flask fitted with a condenser. 4-Bromophenol (26.2 g, 0.15 mol) was added and the solution was allowed to stir for 40 minutes at 65 °C. The clear solution became turbid followed by a colour change to dark rose. 1,3-Dibromopropane (14.13 g, 7.15 ml, 0.07 mol) was added dropwise to the solution and the mixture was set to reflux at 106 °C for 24 hrs, allowed to cool, filtered, and twice washed with 50 ml of $H_2O$ to yield a pure white solid. The desired solid was then allowed to dry under high vacuum and recrystallized from hot ethanol. The resulting colourless crystalline solid was then dried under vacuum for 24 hrs to yield a pure product.

**Yield** 35.4 g (62 %)

**m.p.** 148 ºC

**$^1$H NMR** (400 MHz, $CDCl_3$, 25 °C): δ = 2.24 ppm [q, 2H, $CH_2C\mathbf{H_2}CH_2$], 4.11 ppm [t, 4H, $C\mathbf{H_2}CH_2C\mathbf{H_2}$], 6.78 ppm [dd, 4H, Ar-H], 7.37 ppm [dd, 4H, Ar-H]

**$^{13}$C {$^1$H} NMR** (400 MHz, $CDCl_3$, 25 °C): δ = 29.49 ppm, 64.90 ppm, 113.31 ppm, 116.64 ppm, 132.62 ppm, 158.27 ppm

**EI-MS** (70 eV): m/z (rel. int. %) 386 (45) $[M]^{+\bullet}$, 214 (35), 185 (30), 172 (15), 157 (25), 143 (8), 134 (100), 119 (14), 106 (8), 76 (20), 63 (15)

### 4.1.9 Preparation of 4-(3-Methyl-3-hydroxy-1-butynyl)phenoxy propane – (9)

In a dry, three-neck 250 ml round bottom flask, fitted with a condenser, argon inlet, and glass stopper, was placed a mixture of 1,3-Bis(4-bromophenoxy)propane (6.18 g, 16.0 mmol) in dry diisopropylamine (80 ml) and

dry THF (80 ml). The solution was degassed with argon for 1.5 hrs, 2-methyl-3-butyn-2-ol (10.77 g, 10.50 ml, 0.128 mol) was added, and the reaction was heated to 80 °C. To the clear yellow solution was added triphenylphosphine (1.45 g, 5.53 mmol), Copper(I) iodide (360 mg, 1.89 mmol), and $PdCl_2[P(C_6H_5)_3]_2$ (360 mg, 0.513 mmol) producing a gradual turbidity. The temperature was raised to 105 °C and maintained for 24 hrs, then left to stir under argon for an additional 24 hrs at room temperature. The triethylamine hydrobromide salt was removed by filtration, followed by washing with methylene chloride until the washes were colourless. The triethylamine and $CH_2Cl_2$ were removed in vacuo, leaving a solid orange residue. The residual solid was taken up in $CH_2Cl_2$ (150 ml), washed three times with 10 % $H_2SO_4$, and twice washed with distilled water. The organic layer was the dried over $MgSO_4$, filtered, and the $CH_2Cl_2$ was then removed on a rotary evaporator, leaving an oily orange residue. The oil was subjected to two re-precipitations from $CH_2Cl_2$/ hexane yielding a pure light beige solid product.

| | |
|---|---|
| **Yield** | 4.68 g (74 %) |
| **m.p.** | 120 ºC |
| **$^1$H NMR** | (400 MHz, $CDCl_3$, 25 °C): δ = 1.61 ppm [s, 12H, C**H$_3$**], 2.04 ppm [s, 1H, O**H**], 2.22 ppm [q, 2H, $CH_2C$**H$_2$**$CH_2$], 4.14 ppm [t, 4H, C**H$_2$**$CH_2C$**H$_2$**], 6.82 ppm [d, 4H, Ar-H], 7.34 ppm [d, 4H, Ar-H] |
| **$^{13}$C {$^1$H} NMR** | (400 MHz, $CDCl_3$, 25 °C): δ = 29.51 ppm, 31.92 ppm, 64.71 ppm, 66.00 ppm, 82.32 ppm, 92.55 ppm, 114.93 ppm, 115.29 ppm, 128.85 ppm, 133.44 ppm, 159.13 ppm |
| **EI-MS** | (70 eV): m/z (rel. int. %) 392 (3) $[M]^{+\bullet}$, 359 (5), 277 (55), 262 (100), 217 (3), 201 (17), 183 (65), 159 (8), 152 (10), 133 (6), 115 (6), 108 (30), 84 (10), 77 (15), 59 (5) |

### 4.1.10 Preparation of 1,3-Bis(4-ethynphenoxy)propane – (10)

In a double-neck 1L round bottom flask fitted with a distilling head was placed 4-(3-Methyl-3-hydroxy-1-butynyl)phenoxypropane (4.5 g, 11.46 mmol) in 285 ml of toluene. The reaction mixture was made homogeneous by heating to 70 °C (producing a light orange solution) at which time 115 ml of a 10% NaOH/ $CH_3OH$ solution was added. Toluene was distilled to half its volume at which point a sample was withdrawn and analyzed by TLC (silica, EA: hex / 40: 60). The reaction flask was replenished with toluene and the distillation/ TLC/ addition process was repeated three times. When the reaction was deemed complete by TLC, the remaining toluene was removed by vacuum distillation. The residual dark brown solid was then purified by flash chromatography (silica gel: $CH_2Cl_2$) to get a light tan solid product.

| | |
|---|---|
| **Yield** | 1.40 g (44 %) |
| **m.p.** | 117 ºC |
| **$^1$H NMR** | (400 MHz, $CDCl_3$, 25 °C): δ = 2.26 ppm [q, 2H, $CH_2C\mathbf{H_2}CH_2$], 3.00 ppm [s, 2H, C**H**], 4.15 ppm [t, 4H, $C\mathbf{H_2}CH_2C\mathbf{H_2}$], 6.85 ppm [d, 4H, Ar-H], 7.42 ppm [d, 4H, Ar-H] |
| **$^{13}$C {$^1$H} NMR** | (400 MHz, $CDCl_3$, 25 °C): δ = 29.44 ppm, 64.69 ppm, 76.18 ppm, 83.95 ppm, 114.62 ppm, 114.79 ppm, 133.93 ppm, 159.49 ppm |
| **EI-MS** | (70 eV): m/z (rel. int. %) 276 (100) $[M]^{+\bullet}$, 159 (100), 144 (13), 131 (85), 118 (50), 101 (92), 89 (50), 75 (33), 63 (30) |
| **IR (cm$^{-1}$)** | 540.85, 604.19, 663.85, 696.00, 837.95, 967.20, 986.57, 1054.05, 1096.15, 1111.15, 1171.68, 1244.21, 1288.29, 1384.25, 1472.59, 1506.78, 1568.35, 1603.91, 2107.28, 2953.59, 3293.12 |

### 4.1.11 Preparation of 1,4-Bis(2-ethylhexyl)oxybenzene – (11)

Hydroquinone (10.10 g, 0.091 mol) was dissolved in 100 ml of ethanol and degassed with nitrogen for 30 minutes in a 1L double-neck round bottom flask. KOH (16.3 g, 0.291 mol) was added and the solution was stirred under reflux for 20 minutes. 2-ethylhexylbromide (56.13 g, 0.291 mol) was added dropwise under nitrogen over a period of 45 minutes. The reaction was allowed to proceed for 50 hrs until no further progress could be observed by TLC (silica, EA: hex / 5: 95). The ethanol was then removed by vacuum distillation. The residue was dissolved in $CH_2Cl_2$ and the salts were filtered off by gravity filtration. The resulting $CH_2Cl_2$ solution was then extracted with a 2% NaOH solution (3 × 200 ml). This acidic washing process was not sufficient enough to get rid of the mono-alkylated side product formed in the reaction. The organic solution was extracted with three 100 ml portions of water and allowed to dry over $MgSO_4$. Upon evaporation of the solvent, a dark oil was obtained and subjected to vacuum distillation at 200 °C (0.3 mm Hg) unsuccessfully. The product was chromatographed (silica, EA: Hex / 5: 95) with excellent separation, eluting first from the column.

| | |
|---|---|
| **Yield** | 26 g (85 %) |
| **b.p.** | 165 ºC (0.05 Torr) |
| **$^1$H NMR** | (400 MHz, $CDCl_3$, 25 °C): δ = 0.96 ppm [m, 12H, C**H$_3$**], 1.42 ppm [m, 16H, C**H$_2$**], 1.77 ppm [q, 2H, $OCH_2C$**H$_2$**], 3.82 ppm [d, 4H, OC**H$_2$**], 6.86 ppm [s, 4H, Ar-H] |
| **$^{13}$C {$^1$H} NMR** | (500 MHz, $CDCl_3$, 25 °C): δ = 11.08 ppm, 14.09 ppm, 23.06 ppm, 23.83 ppm, 29.07 ppm, 30.51 ppm, 39.44 ppm, 71.11 ppm, 115.30 ppm, 153.40 ppm |
| **EI-MS** | (70 eV): m/z (rel. int. %) 334 (30) $[M]^{+\bullet}$, 222 (15), 123 (5), 110 (100), 71 (15), 57 (23) |

### 4.1.12 Preparation of 2-Bromo-1,4-bis(2-ethylhexyl)oxybenzene – (12)

1,4-Bis(2-ethylhexyl)oxybenzene (12.01 g, 35.92 mmol) and sodium acetate (2.85 g, 34.81 mmol) were dissolved in 25 mls of acetic acid in a 250 ml round bottom flask. The reaction was cooled to 0 °C. Bromine (5.85 g, 34.8 mmol) was then added slowly at this temperature, with stirring, over a period of six hours using an addition funnel. The solution was then stirred for 24 hrs at room temperature and monitored by TLC (silica, EA: Hex / 5: 95). The mixture was poured into water (50 ml), extracted five times with 25 ml of chloroform, neutralized with a saturated sodium hydrogen carbonate solution, and allowed to dry over $Na_2SO_4$. Upon evaporation of the solvent, a brown oily residue remained, which was subject to column chromatography (silica, 100 % Hexane).

| | |
|---|---|
| **Yield** | 11.65g (78 %) |
| **b.p.** | 141 °C/0.4 mm Hg |
| **$^1$H NMR** | (400 MHz, $CDCl_3$, 25 °C): δ = 0.93 ppm [m, 12H, C**H$_3$**], 1.33 ppm [m, 16H, C**H$_2$**], 1.68 ppm & 1.74 ppm [m, 2H, $OCH_2$C**H**], 3.77 ppm [d, 2H, OC**H$_2$**], 3.84 ppm [d, 2H, OC**H$_2$**], 6.80 ppm [s, 1H, Ar-H], 6.81 ppm [s, 1H, Ar-H], 7.12 ppm [d, 1H, Ar-H] |
| **$^{13}$C {$^1$H} NMR** | (400 MHz, $CDCl_3$, 25 °C): δ = 11.43 ppm, 11.52 ppm, 14.42 ppm, 23.40 ppm, 24.17 ppm, 24.23 ppm, 29.41 ppm, 29.43 ppm, 30.84 ppm, 39.76 ppm, 39.87 ppm, 71.65 ppm, 72.78 ppm, 113.07 ppm, 114.61 ppm, 114.67 ppm, 119.87 ppm, 150.28 ppm, 154.10 ppm |

### 4.1.13 Preparation of 2-Bromo-5-iodo-1, 4-bis(2-ethylhexyl)oxybenzene – (13)

2-Bromo-1,4-bis(2-ethylhexyl)oxybenzene (1 g, 2.42 mmol) was dissolved in acetic acid (1.56 ml) and tetrachloromethane (0.38 ml). To this solution were added iodine (0.61 g), concentrated sulfuric acid (0.19 ml), distilled water (0.1 ml), and finally potassium iodate (0.20 g). The mixture was stirred for 5 h under reflux conditions and monitored via TLC (Hexane). In order to remove excess iodine, $NaHSO_4$ was added until the violet colour of iodine disappeared. The mixture was then poured into ice water (25 ml) and extracted with chloroform. The organic phases were neutralized with saturated sodium bicarbonate and dried with sodium sulfate. The solvent was evaporated and the resulting product was an light yellow oil, pure by $^1$H NMR.

**Yield** 1.07 g ( 82 %)

**b.p.** 164 $^0$C / 0.5 mmHg

**$^1$H NMR** (500 MHz, $CDCl_3$, 25 °C): δ = 0.92 ppm [m, 12H, C**H$_3$**], 1.41 ppm [m, 16H, C**H$_2$**], 1.78 ppm [m, 2H, $OCH_2$C**H**], 3.80 ppm [d, 4H, OC**H$_2$**], 6.98 ppm [s, 1H, Ar-H], 7.27 ppm [s, 1H, Ar-H]

### 4.1.14 Preparation of Monomer – (14)

To a 250 ml oven-dried Schlenk flask was added 2-bromo-5-iodo-1,4-bis(2-ethylhexyl)oxybenzene (3.49 g, 6.47 mmol) under argon. 100 ml of freshly dried and distilled toluene and 25 ml of diisopropylamine were then added and the solution was degassed with argon for 1.5 hrs. The pale yellow solution was then cooled in an ice bath and 5, 5'-diethynyl-2, 2'-bipyridine (0.61 g, 2.94 mmol) was added under argon. $PdCl_2(PPh_3)_2$ (68 mg, 0.097 mmol) and CuI (18.5 mg, 0.097 mmol) were added and the mixture was degassed for 30 minutes. The light

orange coloured solution was then allowed to stir while being cooled in an ice bath for 3 hrs. This reaction mixture was then gradually brought up to room temperature and allowed to stir overnight. The reaction was stopped after a total of 20 hrs. The salts present in the reaction were then filtered off by gravity. One is able to confirm completion of the reaction by TLC (silica, EA: hex/ 5: 95). The solvents were then removed by rotary evaporation and the resulting yellow oil was subject to column chromatography (silica gel; $CH_2Cl_2$) and yielded light yellow crystals.

| | |
|---|---|
| **Yield** | 1.5 g (51%) |
| **m.p.** | 78 ºC |
| **$^1$H NMR** | (250 MHz, $CDCl_3$, 25 °C): δ = 0.95 ppm [m, 24H, C**H$_3$**], 1.51 ppm [m, 32H, C**H$_2$**], 2.12 ppm [q, 4H, $OCH_2C$**H**], 3.89 ppm [d, 8H, OC**H$_2$**], 7.04 ppm [s, 2H, Ar-H], 7.13 ppm [s, 2H, Ar-H], 7.92 ppm [d, 2H, C**H**CN], 8.43 ppm [d, 2H, C**H**CHCN], 8.80 ppm [d, 2H, C**H**N] |
| **$^{13}$C {$^1$H} NMR** | (250 MHz, $CDCl_3$, 25 °C): δ = 11.48 ppm, 14.34 ppm, 23.30 ppm, 24.22 ppm, 29.33 ppm, 30.83 ppm, 39.76 ppm, 72.35 ppm, 72.62 ppm, 90.36 ppm, 91.02 ppm, 111.87 ppm, 114.37 ppm, 117.33 ppm, 117.89 ppm, 120.89 ppm, 121.02 ppm, 139.43 ppm, 149.85 ppm, 151.76 ppm, 154.20 ppm, 154.74 ppm |
| **UV-Vis ($CH_2Cl_2$)** | $\lambda_{max}$/nm= 284, 331, 376 Concentration: 0.287 mg/25 ml ($1.11e^{-5}$ mol/L) |
| **IR ($cm^{-1}$)** | 652.612, 735.571, 793.212, 836.922, 855.345, 924.06, 1028.9, 1122.76, 1212.31, 1272.41, 1378.94, 1456.99, 1490.58, 1591.58, 2213.84, 2858.5, 2924.89, 2959.45 |
| **Elemental Analysis** | C (67.83 %), H (7.65 %), N (2.73 %), Br (15.56 %) = Calculated<br>C (67.27 %), H (8.22 %), N (2.66 %), Br (15.65 %) = Found |
| **Fluorescence** | $\lambda_{max}$ (Excitation) = 383.95 nm, $\lambda_{max}$ (Emission) = 457.98 nm |

### 4.1.15 Preparation of Polymer – (15)

Monomer **14** (0.4554 g, 0.44 mmol), 1,2-bis(4-ethynphenoxy)ethane **7** (0.1163 g, 0.44 mmol), $Pd(PPh_3)_4$ (20.45 mg, 0.0177 mmol, 4 mol %), and CuI (3.37 mg, 0.0177 mmol, 4 mol %) were added to a degassed solution of 15 ml diisopropylamine and 60 ml toluene in a 3-neck round bottom flask. After degassing the reaction mixture for a further 1 hr, it was stirred at 70-75 °C. One can observe the formation of small bright yellow crystals above the solvent level, indicating the formation of hydrobromide salts. After a total reaction time of 68 h, 10 ml of toluene was added and the reaction mixture was transferred to a 250 ml separatory funnel. The mixture was then extracted once with 60 ml of water. Minimal shaking is preferred at this point in the work-up in order to minimize the formation of emulsions. The water layer was then extracted a further three times and the organic layer was dried over magnesium sulfate. The light orange solution was concentrated and added drop-wise to a vigorously stirred and cooled solution of methanol. The precipitate was collected and washed repeatedly with methanol to yield bright orange crystals.

**Yield** 82%

**$^1$H NMR** (300 MHz, $CDCl_3$, 25 °C): δ = 0.94 ppm [m, 24H, C**H$_3$**], 1.51 ppm [m, 32H, C**H$_2$**], 3.94 ppm [d, 8H, OC**H$_2$**Ethhex], 4.37 ppm [s, 4H, OC**H$_2$CH$_2$**O], 6.89 ppm [d, 4H, Ar-H (C2 spacer)], 7.04 ppm [s, 2H, Ar-H], 7.13 ppm [s, 2H, Ar-H], 7.42 ppm [d, 4H, Ar-H (C2 spcaer)], 7.84 ppm [d, 2H, Bipyr-H], 8.34 ppm [d, 2H, Bipyr-H], 8.74 ppm [d, 2H, Bipyr-H]

**$^{13}$C {$^1$H} NMR** (300 MHz, $CDCl_3$, 25 °C): δ = 11.66 ppm, 14.46 ppm, 23.43 ppm, 24.39 ppm, 29.51 ppm, 31.03 ppm, 39.97 ppm, 66.81 ppm, 72.36 ppm, 85.22 ppm, 91.09 ppm, 91.88 ppm, 95.51 ppm, 112.91 ppm, 115.04 ppm, 116.48 ppm, 116.83 ppm, 120.96 ppm, 133.42 ppm, 134.45 ppm, 139.49 ppm, 151.93 ppm, 153.99 ppm, 154.40 ppm, 159.00 ppm

**UV-Vis ($CH_2Cl_2$)** $\lambda_{max}$/nm= 319, 341, 400 Concentration: 0.297 mg/25 ml ($1.05e^{-5}$ mol/L)

| | |
|---|---|
| **IR ($cm^{-1}$)** | 651.747, 736.713, 800.60, 827.136, 928.105, 1023.85, 1171.47, 1212.19, 1240.56, 1277.95, 1378.67, 1413.52, 1460.35, 1510.75, 1600.67, 2205.57, 2859.40, 2926.13, 2957.68 |
| **Elemental Analysis** | C (80.96 %), H (8.05 %), N (2.48 %) = Calculated<br>C ( 76.87 %), H (7.49 %), N (2.10 %) = Found |
| **GPC (THF)** | $M_n$: $8.7358e^3$ g/mol, $M_w$: $1.5470e^4$ g/mol, $M_z$: $2.0966e^4$ g/mol, $M_v$: $1.4694e^4$ g/mol, polydispersity index = 1.77 |
| **Fluorescence** | $\lambda_{max}$ (Excitation) = 397. nm, $\lambda_{max}$ (Emission) = 485 nm |

### 4.1.16 Preparation of 2-Bromohydroquinone – (16)

To a cooled three-neck round bottom flask with mechanical stirring, containing a suspension of hydroquinone (50 g, 0.45 mol) in 300 ml of *tert*-butyl methyl ether, was added bromine (23 ml, 0.45 mol) in 400 ml of *tert*-butyl methyl ether. The drop-wise addition of bromine was conducted at -13 to – 20 °C in order to minimize di-bromination, and was allowed to proceed over a 5-hour period. One could observe the colour of the reaction slush change from white to yellow to orange. The bright orange reaction mixture was then gradually brought up to room temperature over a period of 2 hours, with stirring, then allowed to stand overnight. The *tert*-butyl methyl ether was then removed by distillation and rotary evaporation. The product was left to crystallize in the fridge over a three-day period then recrystallized from ethanol.

| | |
|---|---|
| **Yield** | 30.10 g (35 %) |
| **m.p.** | 111 ºC |
| **$^{1}$H NMR** | (200 MHz, $d_6$-Acetone, 25 °C): δ = 6.69 ppm [d, 1H, Ar-H], 6.85 ppm [d, 1H, Ar-H], 7.01 ppm [s, 1H, Ar-H], 8.11 ppm [s, 2H, O**H**] |
| **$^{13}$C {$^{1}$H} NMR** | (200 MHz, $d_6$-Acetone, 25 °C): δ = 110.62 ppm, 116.78 ppm, 118.12 ppm, 120.39 ppm, 148.30 ppm, 151.54 ppm |

### 4.1.17 Preparation of 2-Bromo-1,4-bis(dodecyl)oxybenzene – (17)

1,4-bis(dodecyl)oxybenzene (10 g, 0.0224 mol) was dissolved in 75 mls of glacial acetic acid with the aid of slight heating. Sodium acetate (1.78 g, 0.0217 mol) was added to the solution with stirring. The stirring was allowed to continue for 15 minutes in order to insure complete solubilization. The mixture was then cooled in an ice bath and allowed to stir for a further 30 minutes. Bromine (3.47 g, 0.0217 mol) was then added dropwise to the cooled solution, with stirring. The mixture was then allowed to warm to room temperature over a four-hour period and stirred overnight at room temperature. The acetic acid was distilled under vacuum and the residue was taken up in methylene chloride. The organic phase was washed twice with a concentrated sodium sulfite solution, followed by two water washings. The organic phase was then dried over sodium sulfate. The methylene chloride was evaporated and the residue was recrystallized from methylene chloride/hexane (5:1) to yield a colourless crystalline product.

| | |
|---|---|
| **Yield** | 10 g (85 %) |
| **m.p.** | 59 ºC |
| **$^{1}$H NMR** | (400 MHz, $CDCl_3$, 25 °C): δ = 0.88 ppm [t, 6H, C**H$_3$**], 1.30 ppm [m, 18H, C**H$_2$**], 1.79 ppm [q, 4H, $OCH_2C$**H$_2$**], 3.88 ppm [t, 2H, OC**H$_2$**], 3.95 ppm [t, 2H, OC**H$_2$**], 6.78 ppm [s, 1H, Ar-H], 6.81 ppm [s, 1H, Ar-H], 7.11 ppm [s, 1H, Ar-H] |
| **$^{13}$C {$^{1}$H} NMR** | (400 MHz, $CDCl_3$, 25 °C): δ =14.11 ppm, 22.68 ppm, 25.99 ppm, 29.25 ppm, 29.27 ppm, 29.34 ppm, 29.56 ppm, 29.58 ppm, 29.63 ppm, 29.65 ppm, 31.91 ppm, 68.82 ppm, 70.23 ppm, 114.38 ppm, 114.72 ppm, 119.48 ppm, 149.76 ppm, 153.58 ppm |
| **EI-MS** | (70 eV): m/z (rel. int. %) 526 (85) $[M]^{+\bullet}$, 446 (30), 358 (32), 188 (100), 110 (44), 97 (17), 83 (30), 69 (54), 56 (70) |

### 4.1.18 Preparation of 2-Bromo-5-iodo-1,4-bis(dodecyl)oxybenzene – (18)

2-Bromo-1,4-bis(dodecyl)oxybenzene (20 g, 0.038 mol) was dissolved in 320 mls of glacial acetic acid. In a separate flask, 3.1 mls of sulfuric acid was added to 13.9 mls of distilled water. The acid/water mixture was then added to the solution of the mono-brominated compound. The mixture was heated to 60 ºC with stirring. Iodine crystals (11.48 g, 0.0452 mol), potassium iodate (3.36 g, 0.0156 mol), and $CCl_4$ (20 mls) were then added and the mixture was heated to an oil bath temperature of 120 ºC. After 30 hours the mixture was cooled and the glacial acetic acid was distilled under vacuum. The residue was dissolved in methylene chloride and washed with a sodium carbonate solution, then a sodium sulfite solution, and finally with water. The organic layer was dried over sodium sulfate and the solvent was evaporated. The residue was recrystallized from methylene chloride and hexane (9:1) to yield a white crystalline solid.

| | |
|---|---|
| **Yield** | 20.35 g (82 %) |
| **m.p.** | 75 ºC |
| **$^1$H NMR** | (200 MHz, $CDCl_3$, 25 °C): δ = 0.88 ppm [t, 6H, C**H$_3$**], 1.27 ppm & 1.47 ppm & 1.79 ppm [m, 40H, C**H$_2$**], 3.93 ppm [t, 4H, OC**H$_2$**], 6.98 ppm [s, 1H, Ar-H], 7.27 ppm [s, 1H, Ar-H] |
| **$^{13}$C {$^1$H} NMR** | (200 MHz, $CDCl_3$, 25 °C): δ = 14.38 ppm, 22.94 ppm, 26.17 ppm, 26.27 ppm, 29.35 ppm, 29.39 ppm, 29.52 ppm, 29.55 ppm, 29.61 ppm, 29.80 ppm, 29.83 ppm, 29.89 ppm, 29.92 ppm, 32.16 ppm, 70.52 ppm, 70.58 ppm, 82.50 ppm, 112.62 ppm, 117.27 ppm, 124.42 ppm, 150.96 ppm, 152.75 ppm |
| **EI-MS** | (70 eV): m/z (rel. int. %) 652 (95) $[M]^{+\bullet}$, 482 (15), 362 (10), 314 (100), 268 (10), 188 (20), 97 (25), 83 (42), 69 (77), 58 (100) |

### 4.1.19 Preparation of 1-Bromo-2,5-bis(dodecyl)-4-trimethylsilylethynylbenzene – (19)

2-Bromo-5-iodo-1,4-bis(dodecyl)oxybenzene (5 g, 7.69 mmol) and a catalyst mixture of bis(tetraphenylphosphane)palladium dichloride (131.5 mg, 0.1875 mmol), copper(I) iodide (71.4 mg, 0.375 mmol), and triphenylphosphine (98.25 mg, 0.375 mmol) was dissolved in dry piperidine (30 ml) and the system was flushed with argon. Trimethylsilylacetylene (0.827 g, 8.44 mmol) was added to the solution in small fractions. After the solution had stirred for 2.5 h, the solvent was evaporated. The product was purified by column chromatography (silica/ $CH_2Cl_2$:Hexane/ 1:20) to yield a pure dark red solid.

**Yield** 0.9 g

**$^1$H NMR** (500 MHz, $CDCl_3$, 25 °C): δ = 0.25 ppm [s, 9H, $(CH_3)_3Si$], 0.88 ppm [t, 6H, $CH_3$], 1.27 ppm & 1.47 ppm & 1.79 ppm [m, 40H, $CH_2$], 3.93 ppm [t, 4H, $OCH_2$], 6.94 ppm [s, 1H, Ar-H], 7.04 ppm [s, 1H, Ar-H]

### 4.1.20 Preparation of 1-Bromo-4-ethynyl-2, 5-bis(dodecyl)oxybenzene – (20)

1-Bromo-2,5-bis(dodecyl)-4-trimethylsilylethynylbenzene (6 g, 9.62 mmol) was dissolved in 150 ml of methanol and 3.4 ml of a sodium hydroxide solution (10 g NaOH in 50 ml water). After the solution had stirred for 30 minutes, a white precipitate was observed which proved to be the pure desired product.

**Yield** 5.30 g (75 %)

**$^1$H NMR** (500 MHz, $CDCl_3$, 25 °C): δ = 0.88 ppm [t, 6H, $CH_3$], 1.27 ppm & 1.47 ppm & 1.79 ppm [m, 40H, $CH_2$], 3.28 ppm [s, 1H, CCH], 3.95 ppm & 3.96 ppm [d of t, 4H, $OCH_2$], 6.97 ppm [s, 1H, Ar-H], 7.08 ppm

[s, 1H, Ar-H]

**$^{13}C\{^{1}H\}$ NMR** (500 MHz, $CDCl_3$, 25 °C): δ = 14.47 ppm, 23.04 ppm, 26.22 ppm, 26.30 ppm, 29.44 ppm, 29.50 ppm, 29.66 ppm, 29.70 ppm, 29.90 ppm, 29.93 ppm, 29.99 ppm, 30.00 ppm, 32.27 ppm, 70.23 ppm, 70.47 ppm, 79.88 ppm, 81.91 ppm, 111.63 ppm, 114.31 ppm, 118.31 ppm, 118.73 ppm, 149.68 ppm, 155.06 ppm

**EI-MS** (70 eV): m/z (rel. int. %) 550 (90) $[M]^{+\bullet}$, 382 (10), 212 (100), 134 (12), 97 (10), 83 (17), 69 (37), 58 (54)

### 4.1.21 Preparation of Monomer – (21)

To a 250 ml oven-dried Schlenk flask was added 2-Bromo-5-iodo-1,4-bis(dodecyl)oxybenzene **18** (2.67 g, 4.10 mmol) under argon. 65 ml of freshly dried and distilled toluene and 16 ml of diisopropylamine were then added and the solution was degassed with argon for 1 hr. 5, 5'-diethynyl-2,2'-bipyridine **4** (380 mg, 1.86 mmol) was added under argon with cooling and degassed for an additional 20 minutes. $PdCl_2(PPh_3)_2$ (45 mg, 0.061 mmol, 1.5 mol %) and CuI (13 mg, 0.061 mmol, 1.5 mol %) were then added. The solution was then allowed to stir for 3 hours at 0 °C and gradually brought up to room temperature overnight. The reaction was complete after 18 hours (TLC/$CH_2Cl_2$). The reaction mixture was brought to room temperature and filtered by gravity. The solvents were evaporated in vacuo. The brown residue was taken up in methylene chloride and extracted four times with water. The organic phase was dried over sodium sulfate and the methylene chloride was evaporated. The resulting solid was then subjected to column chromatography with Hexane/Ethyl Acetate (90:10). The desired monomer eluted first from the column with a larger molecular weight compound eluting last. A solid orange product was obtained.

| | |
|---|---|
| **Yield** | 1.14 g (22 %) |
| **m.p.** | 85 ºC |
| **$^1$H NMR** | (500 MHz, $CDCl_3$, 25 °C): δ = 0.88 ppm [m, 12H, C**H$_3$**], 1.40 ppm [m, 80H, C**H$_2$**], 1.83 ppm [qt, 8H, C**H$_2$**], 4.01 ppm [dt, 8H, OC**H$_2$**], 7.04 ppm [s, 2H, Ar-H], 7.13 ppm [s, 2H, Ar-H], 7.92 ppm [d, 2H, C**H**CN], 8.43 ppm [d, 2H, C**H**CHCN], 8.80 ppm [d, 2H, C**H**N] |
| **$^{13}$C {$^1$H} NMR** | (500 MHz, $CDCl_3$, 25 °C): δ = 14.34 ppm, 22.91 ppm, 26.24 ppm, 29.41 ppm, 29.43 ppm, 29.45 ppm, 29.54 ppm, 29.55 ppm, 29.58 ppm, 29.60 ppm, 29.64 ppm, 29.77 ppm, 32.13 ppm, 70.07 ppm, 70.10 ppm, 90.16 ppm, 91.14 ppm, 117.71 ppm, 117.72 ppm, 118.19 ppm, 118.21 ppm, 120.78 ppm, 120.80 ppm, 120.89 ppm, 139.37 ppm, 139.38 ppm, 149.73 ppm, 149.74 ppm, 151.86 ppm, 154.30 ppm, 154.31 ppm, 154.55 ppm |
| **UV-Vis ($CH_2Cl_2$)** | $\lambda_{max}$/nm = 285, 373 Concentration: 1.0e$^{-5}$ mol/L |
| **Elemental Analysis** | C (71.02 %), H (8.86 %), N (2.24 %) = Calculated<br>C (70.91 %), H (8.70 %), N (2.16 %) = Actual |
| **Fluorescence** | $\lambda_{max}$ (Excitation) = 381.57 nm, $\lambda_{max}$ (Emission) = 453.77 nm |

### 4.1.22 Preparation of 1,4-bis(dodecyl)oxybenzene – (22)

Hydroquinone (30 g, 0.2727 mol) was dissolved in 200 mls of ethanol. The ethanolic solution was degassed with argon for 30 minutes. Sodium hydroxide pellets (11.97 g, 0.2992 mol) were added to the solution under argon. The mixture was then heated for 2 hours at an oil bath temperature of 80 ºC, in order to solubilize the NaOH pellets. 1-Bromododecane (149.5 g, 143.75 ml, 0.599 mol) was then added under argon and the mixture was allowed to stir for 24 hours and heat at an oil bath temperature of 95 ºC. The mixture was then filtered and recrystallized twice from ethanol to yield a colourless crystalline solid.

| | |
|---|---|
| **Yield** | 96 g (79 %) |
| **m.p.** | 79 ºC |
| **$^{1}$H NMR** | (400 MHz, $CDCl_3$, 25 °C): δ = 0.87 ppm [t, 6H, C**H$_3$**], 1.30 ppm & 1.76 ppm [m, 40H, C**H$_2$**], 3.89 ppm [t, 4H, OC**H$_2$**], 6.82 ppm [s, 4H, Ar-H] |
| **$^{13}$C {$^{1}$H} NMR** | (400 MHz, $CDCl_3$, 25 °C): δ =14.47 ppm, 23.05 ppm, 26.42 ppm, 29.70 ppm, 29.77 ppm, 29.78 ppm, 29.95 ppm, 29.99 ppm, 30.02 ppm, 32.28 ppm, 69.03 ppm, 115.75 ppm, 153.56 ppm |
| **EI-MS** | (70 eV): m/z (rel. int. %) 446 (100) $[M]^{+\bullet}$, 278 (15), 123 (7), 110 (92), 97 (7), 83 (11), 69 (20) |

### 4.1.23 Preparation of 1,4-Bis(hexyl)oxybenzene – (24)

Hydroquinone (10.10 g, 0.091 mol) was dissolved in 100 ml of ethanol and degassed with nitrogen for 30 minutes in a 1L double-neck round bottom flask. KOH (16.3 g, 0.291 mol) was added and the solution was stirred under reflux for 20 minutes. 1-bromohexane (48.04 g, 0.291 mol) was added dropwise under nitrogen over a period of 45 minutes. The reaction was allowed to proceed for 50 hrs until no further progress could be observed by TLC (silica, EA: hex / 5: 95). The reaction mixture was then filtered and the crude product was twice recrystallized from ethanol.

| | |
|---|---|
| **Yield** | 25 g (88 %) |
| **m.p.** | 45 ºC |
| **$^{1}$H NMR** | (400 MHz, $CDCl_3$, 25 °C): δ = 0.90 ppm [t, 6H, C**H$_3$**], 1.34 ppm [m, 12H, C**H$_2$**], 1.74 ppm [q, 4H, $OCH_2C$**H$_2$**], 3.89 ppm [t, 4H, OC**H$_2$**], 6.81 ppm [s, 4H, Ar-H] |
| **$^{13}$C {$^{1}$H} NMR** | (400 MHz, $CDCl_3$, 25 °C): δ = 14.27 ppm, 22.85 ppm, 25.98 ppm, 29.61 ppm, 31.85 ppm, 68.89 ppm, 115.62 ppm, 153.44 ppm |
| **EI-MS** | (70 eV): m/z (rel. int. %) 278 (60) $[M]^{+\bullet}$, 194 (20), 110 (100), 55 (12) |

### 4.1.24 Preparation of 2-Bromo-1,4-bis(hexyl)oxybenzene – (25)

1,4-bis(hexyl)oxybenzene (6.24 g, 0.0224 mol) was dissolved in 75 mls of glacial acetic acid with the aid of slight heating. Sodium acetate (1.78 g, 0.0217 mol) was added to the solution with stirring. The stirring was allowed to continue for 15 minutes in order to insure complete solubilization. The mixture was then cooled in an ice bath and allowed to stir for a further 30 minutes. Bromine (3.47 g, 0.0217 mol) was then added dropwise to the cooled solution, with stirring. The mixture was then allowed to warm to room

temperature over a four-hour period and stirred overnight at room temperature. The acetic acid was distilled under vacuum and the residue was taken up in methylene chloride. The organic phase was washed twice with a concentrated sodium sulfite solution, followed by two water washings. The organic phase was then dried over sodium sulfate. The methylene chloride was evaporated and the residue was distilled in vacuum.

| | |
|---|---|
| **Yield** | (78 %) |
| **b.p.** | 176 $^0$C/ 0.5 mm Hg |
| **$^1$H NMR** | (400 MHz, $CDCl_3$, 25 °C): δ = 0.90 ppm [t, 6H, C**H$_3$**], 1.33 ppm [m, 12H, C**H$_2$**], 1.76 ppm [q, 4H, $OCH_2C$**H$_2$**], 3.87 ppm [t, 2H, OC**H$_2$**], 3.94 ppm [t, 2H, OC**H$_2$**], 6.78 ppm [m, 2H, Ar-H], 7.10 ppm [d, 1H, Ar-H] |
| **$^{13}$C {$^1$H} NMR** | (400 MHz, $CDCl_3$, 25 °C): δ = 14.27 ppm, 22.83 ppm, 25.92 ppm, 29.49 ppm, 31.80 ppm, 69.73 ppm, 77.28 ppm, 113.03 ppm, 114.58 ppm, 114.94 ppm, 115.61 ppm, 119.73 ppm, 150.01 ppm, 153.83 ppm |
| **EI-MS** | (70 eV): m/z (rel. int. %) 358 (85) $[M]^{+\bullet}$, 278 (20), 272 (35), 188 (100), 110 (24), 85 (23), 55 (27) |

### 4.1.25 Preparation of 2-Bromo-5-iodo-1,4-bis(hexyl)oxybenzene – (26)

2-Bromo-1,4-bis(hexyl)oxybenzene (13.60 g, 0.038 mol) was dissolved in 320 mls of glacial acetic acid. In a separate flask, 3.1 mls of sulfuric acid was added to 13.9 mls of distilled water. The acid/water mixture was then added to the solution of the mono-brominated compound. The mixture was heated to 60 ºC with stirring. Iodine crystals (11.48 g, 0.0452 mol), potassium iodate (3.36 g, 0.0156 mol), and $CCl_4$ (20 mls) were then added and the mixture was heated to an oil bath temperature of 120 ºC. After 30 hours the mixture was cooled and the glacial acetic acid was distilled under vacuum. The residue was dissolved in methylene chloride and washed with a sodium carbonate solution, then a sodium sulfite solution, and finally with water. The organic layer was

dried over sodium sulfate and the solvent was evaporated. The residue was recrystallized from methylene chloride and hexane (9:1) to yield a white crystalline solid.

| | |
|---|---|
| **Yield** | 14 g (76 %) |
| **m.p.** | 54 ºC |
| **$^1$H NMR** | (400 MHz, $CDCl_3$, 25 °C): δ = 0.91 ppm [t, 6H, C**H$_3$**], 1.33 ppm & 1.47 ppm [m, 12H, C**H$_2$**], 1.77 ppm [q, 4H, $OCH_2C$**H$_2$**], 3.93 ppm [dt, 4H, OC**H$_2$**], 6.98 ppm [s, 1H, Ar-H], 7.27 ppm [s, 1H, Ar-H] |
| **$^{13}$C {$^1$H} NMR** | (400 MHz, $CDCl_3$, 25 °C): δ = 14.26 ppm, 22.80 ppm, 25.85 ppm, 29.29 ppm, 31.68 ppm, 70.54 ppm, 85.02 ppm, 112.75 ppm, 117.30 ppm, 124.48 ppm, 150.65 ppm, 152.78 ppm |
| **EI-MS** | (70 eV): m/z (rel. int. %) 482 (47) $[M]^{+\bullet}$, 398 (17), 362 (15), 314 (100), 268 (20), 85 (12), 57 (36) |

### 4.1.26 Preparation of Monomer – (27)

To a 250 ml oven-dried Schlenk flask was added 2-bromo-5-iodo-1,4-bis(hexyl)oxybenzene **26** (0.592 g, 0.00122 mol) under argon. 20 ml of freshly dried and distilled toluene and 5 ml of diisopropylamine were then added and the solution was degassed with argon for 1.5 hrs. The pale yellow solution was then cooled in an ice bath and 5, 5'-diethynyl-2, 2'-bipyridine (0.100 g, 0.49 mmol) was added under argon. $PdCl_2(PPh_3)_2$ (13 mg, 0.0183 mmol, 1.5 mol %) and CuI (4 mg, 0.0183 mmol) were added and the mixture was degassed for 30 minutes. The light orange coloured solution was then allowed to stir while being cooled in an ice bath for 3 hrs. This reaction mixture was then gradually brought up to room temperature and allowed to stir overnight. The reaction was stopped after a total of 24 hrs. The salts present in the reaction were then filtered off by gravity. One is able to confirm completion of the reaction by TLC (silica, EA: hex/ 5: 95). The solvents were then removed by rotary evaporation and the resulting yellow oil

was subject to column chromatography (silica gel; $CH_2Cl_2$) and yielded light yellow crystals with the desired product eluting first.

| | |
|---|---|
| **Yield** | 0.23 g ( 54 %) |
| **m.p.** | 145 ºC |
| **$^1$H NMR** | (400 MHz, $CDCl_3$, 25 °C): δ = 0.91 ppm [m, 12H, C**H$_3$**], 1.46 ppm [m, 24H, C**H$_2$**], 1.83 ppm [q, 8H, $OCH_2C$**H$_2$**], 4.01 ppm [m, 8H, OC**H$_2$**], 7.04 ppm [s, 2H, Ar-H], 7.13 ppm [s, 2H, Ar-H], 7.94 ppm [d, 2H, C**H**CN], 8.41 ppm [d, 2H, C**H**CHCN], 8.81 ppm [d, 2H, C**H**N] |
| **$^{13}$C {$^1$H} NMR** | (400 MHz, $CDCl_3$, 25 °C): δ = 14.24 ppm, 22.81 ppm, 22.84 ppm, 25.87 ppm, 25.90 ppm, 29.36 ppm, 29.40 ppm, 31.73 ppm, 31.74 ppm, 70.04 ppm, 70.39 ppm, 90.16 ppm, 91.12 ppm, 112.01 ppm, 114.37 ppm, 117.71 ppm, 118.16 ppm, 120.79 ppm, 120.89 ppm, 139.39 ppm, 149.72 ppm, 151.84 ppm, 154.30 ppm, 154.54 ppm |
| **UV-Vis ($CH_2Cl_2$)** | $\lambda_{max}$/nm = 285, 326, 371 Concentration: 2.22e$^{-5}$ mol/L |
| **Elemental Analysis** | C (65.64 %), H (6.83 %), N (3.06 %) = Calculated<br>C (66.42 %), H (6.96 %), N (2.86 %) = Actual |
| **Fluorescence** | $\lambda_{max}$ (Excitation) = 379.41 nm<br>$\lambda_{max}$ (Emission) = 454.14 nm |

### 4.1.27 Preparation of 5-Bromo-5'-(3-Methyl-3-hydroxy-1-butynyl)-2,2'-bipyridine - (32)

To a 250 ml oven-dried Schlenk flask was added 5,5'-Dibromo-2,2'-bipyridine **(2)** ( 1.00 g, 0.003 mol) under argon. 120 ml of freshly dried and distilled THF and 32 ml of diisopropylamine were then added and the solution was degassed with argon for 1.5 hrs. 2-Methyl-3-butyn-2-ol (0.31 ml, 0.003 mol) was added under argon. $PdCl_2(PPh_3)_2$ (223 mg, 0.318 mmol, 10 mol % per molecule) and CuI (61 mg, 0.318 mmol, 10 mol % per molecule) were added. The

solution was then allowed to stir at 80 ºC for 45 minutes. This reaction mixture was then heated at 50 ºC for 4 hours and gradually brought up to room temperature and allowed to stir overnight and for a total of 24 hours. The reaction mixture was then filtered and the solvent was evaporated in vacuo. The residual solid was subjected to column chromatography ($CH_2Cl_2$/EtOH : 97/3).

**Yield** 0.29 g (31 %)

**m.p.** 107 ºC

**$^1$H NMR** (400 MHz, $CDCl_3$, 25 °C): δ = 1.65 ppm [s, 6H, C**H$_3$**], 2.13 [s, 1H, O**H**], 7.82 ppm [dd, 1H, Bipyr-H], 7.93 ppm [dd, 1H, Bipyr-H], 8.32 [t, 2H, Bipyr-H], 8.69 ppm [dd, 2H, Bipyr-H]

**$^{13}$C {$^1$H} NMR** (400 MHz, $CDCl_3$, 25 °C): δ = 31.35 ppm, 65.67 ppm, 79.03 ppm, 98.40 ppm, 120.00 ppm, 120.21 ppm, 121.38 ppm, 122.58 ppm, 139.54 ppm, 139.61 ppm, 150.26 ppm, 151.66 ppm, 153.81 ppm, 153.86 ppm

**EI-MS** (70 eV): m/z (rel. int. %) 318 (50) $[M]^{+\bullet}$, 301 (100), 273 (17), 259 (26), 75 (10)

### 4.1.28 Preparation of Monomer - (33)

To a 100 ml oven-dried Schlenk flask was added 5-Bromo-5'-(3-Methyl-3-hydroxy-1-butynyl)-2,2'-bipyridine - **(32)** ( 0.040 g, 0.126 mmol) under argon. 25 ml of freshly dried and distilled THF and 6 ml of diisopropylamine were then added and the solution was degassed with argon for 45 minutes. 1,2-Bis(4-ethynphenoxy)ethane **(7)** (16 mg, 0.060 mmol) was added under argon. $PdCl_2(PPh_3)_2$ (5 mg, 0.006 mmol, 5 mol % per molecule) and CuI (1 mg, 0.006 mmol, 5 mol % per molecule). The mixture was set to heat at 65 ºC for 2 days. The observed precipitate was filtered and washed with methylene chloride. The solid was dried under vacuum and submitted for analysis. The material is insoluble in any solvent.

**Yield** 0.3 g ( 68 % )

**m.p.** 158 $^0$C

**MALDI-TOF (CHCA Matrix)** (Pulse Voltage: 2009 V, MCP Voltage: 2350 V) m/z (rel. int. %) 735.5 (100) $[M+1]^{+\bullet}$

### 4.1.29 Preparation of Polymer – (36)

To a 100 ml oven-dried Schlenk flask was added Monomer **14** (200 mg, 0.195 mmol) in 20 ml of dry toluene and 8 ml of diisopropylamine. The solution was allowed to degas for 1 hour. 1,3-bis(4-ethynphenoxy)propane **10** (54 mg, 0.195 mmol) was then added, followed by $Pd(PPh_3)_4$ (9 mg, 0.008 mmol, 4 mol %) and CuI (2 mg, 0.008 mmol, 4 mol %). The reaction was then allowed to stir at 75 ºC for 4 days. The mixture was then transferred to a separatory funnel via the addition of 10 ml of toluene, and extracted three times with water. The organic layer was then dried with sodium sulfate and the solvent was concentrated under vaccum to a total volume of 1-2 mls. The light orange solution was added drop-wise to a vigorously stirred and cooled solution of methanol. The precipitate was collected and washed repeatedly (via Soxhlett) with methanol to yield bright orange crystals.

**Yield** ( 78 % )

**$^1$H NMR** (400 MHz, $CDCl_3$, 25 °C): δ = 0.96 ppm [m, 24H, C**H$_3$**], 1.52 ppm [m, 32H, C**H$_2$**], 2.29 ppm [q, 2H, $OCH_2C$**H$_2$**$CH_2$], 3.91 ppm [m, 8H, OC**H$_2$**Ethhex], 4.18 ppm [s, 4H, OC**H$_2$**$CH_2C$**H$_2$**O], 6.89 ppm [m, 4H, Ar-H (C3 spacer)], 7.03 ppm [s, 2H, Ar-H], 7.13 ppm [s, 2H, Ar-H], 7.46 ppm [m, 4H, Ar-H (C3 spacer)], 7.91 ppm [d, 2H, Bipyr-H], 8.41 ppm [d, 2H, Bipyr-H], 8.81 ppm [d, 2H, Bipyr-H]

**$^{13}$C {$^1$H} NMR** (400 MHz, $CDCl_3$, 25 °C): δ = 11.41 ppm, 14.33 ppm, 23.31 ppm,

| | |
|---|---|
| | 24.28 ppm, 29.35 ppm, 30.89 ppm, 39.80 ppm, 64.60 ppm, 72.36 ppm, 81.45 ppm, 84.95 ppm, 91.08 ppm, 95.52 ppm, 111.90 ppm, 112.73 ppm, 115.36 ppm, 116.56 ppm, 116.75 ppm, 117.35 ppm, 117.90 ppm, 120.84 ppm, 133.28 ppm, 134.29 ppm, 139.35 ppm, 149.85 ppm, 151.80 ppm, 153.89 ppm, 154.30 ppm, 154.75 ppm, 159.15 ppm, 159.68 ppm |
| **UV-Vis ($CH_2Cl_2$)** | $\lambda_{max}$/nm = 283, 303, 321, 344, 381, 391 Concentration: 1.6e$^{-5}$ mol/L |
| **Elemental Analysis** | C (81.01 %), H (8.12 %), N (2.45 %), = Calculated<br>C (74.73 %), H (7.67 %), N (2.48 %) = Actual |
| **GPC (THF)** | $M_n$: 12,005 g/mol, $M_w$: 21,393 g/mol<br>polydispersity index = 1.78 |
| **Fluorescence** | $\lambda_{max}$ (Excitation) = 336.00 nm, 392.42 nm<br>$\lambda_{max}$ (Emission) = 479.71 nm |

### 4.1.30 Preparation of Monomer - (33-B)

To 250 ml oven-dried Schlenk flask was added **32** (170 mg, 0.536 mmol) in 75 ml of dry THF and 15 ml of dry diisopropylamine. The solution was allowed to degas for 1.5 hrs. 1,3-bis(4-ethynphenoxy)propane **10** (71 mg, 0.255 mmol) was added to the degassed solution followed by $PdCl_2(PPh_3)_2$ (19 mg, 0.027 mmol, 5 mol %) and CuI (5 mg, 0.027 mmol, 5 mol %). The mixture was allowed to react at 70 ºC for 3 days. The solvent was then removed under vacuum and the residue was dissolved in methylene chloride. The organic solution was washed with a saturated solution of ammonium chloride, followed by three water washes. The organic phase was dried over sodium sulfate and evaporated to dryness.

| | |
|---|---|
| **Yield** | 0.105 g ( 55 % ) |
| **m.p.** | 111 $^0$C |

| | |
|---|---|
| **MALDI-TOF (CHCA Matrix)** | (Pulse Voltage: 2009 V, MCP Voltage: 2350 V) m/z (rel. int. %) 748.5 (40) $[M]^{+\bullet}$, 749.5 (50) $[M+1]^{+\bullet}$ |

### 4.1.31 Preparation of Monomer - (34-B)

**33-B** ( 0.105g ) was dissolved in 10 ml toluene. 4 eq. 0.022g of NaOH were added and the mixture was heated at 130 ºC for 3 days. The solvent was evaporated and the residue was dissolved in methylene chloride. The solution was then washed with a saturated solution of ammonium chloride and washed three times with water. The organic phase was then dried over sodium sulfate and finally evaporated to dryness.

| | |
|---|---|
| **Yield** | 0.0399 g ( 45 %) |
| **m.p** | 86 $^0$C |
| **$^1$H NMR** | (400 MHz, $CDCl_3$, 25 °C): δ = see figure 17, Chapter 3.4.2 |
| **MALDI-TOF (CHCA Matrix)** | (Pulse Voltage: 2009 V, MCP Voltage: 2350 V) m/z (rel. int. %) 633.3 (30) $[M]^{+\bullet}$, 634.3 (15) $[M+1]^{+\bullet}$ |

### 4.1.32 Preparation of Polymer - (35-B)

To a 100 ml oven-dried Schlenk flask was added Monomer **27** (54 mg, 0.059 mmol) in 12 ml of dry toluene and 5 ml diisopropylamine. The solution was degassed for 1 hr. Monomer **34-B** (37 mg, 0.059 mmol) was then added followed by $Pd(PPh_3)_4$ (4 mg, 0.0029 mmol, 5 mol %) and CuI (1 mg, 0.0029 mmol, 5 mol %). The reaction was allowed to proceed at 80 ºC for four days. The mixture was then transferred to a separatory funnel via the addition of 30 ml of toluene and

extracted with water three times. The organic phase was then dried over magnesium sulfate and concentrated to yield a khaki green solid.

| | |
|---|---|
| **Yield** | ( 68 % ) |
| **$^1$H NMR** | (MHz, $CDCl_3$, 25 °C): δ = see figure 17, Chapter 3.4.2 |
| **UV-Vis ($CH_2Cl_2$)** | $\lambda_{max}$/nm = 381 Concentration: $7e^{-7}$ mol/L |
| **GPC (THF)** | $M_n$: 5,200 g/mol, $M_w$: 6,565 g/mol<br>polydispersity index = 1.34 |
| **Fluorescence** | $\lambda_{max}$ (Excitation) = 349.61 nm, 392.31<br>$\lambda_{max}$ (Emission) = 460.42 nm |

### 4.1.33 Isolation of Monomer – (38)

| | |
|---|---|
| **$^1$H NMR** | (400 MHz, $CDCl_3$, 25 °C): δ = 0.91 ppm [m, 18 H, C**H$_3$**], 1.51 ppm [m, 48 H, C**H$_2$**], 4.00 ppm [q, 8H, OC**H$_2$** end units], 4.08 ppm [t, 4H, OC**H$_2$** center unit], 7.05 ppm [s, 2H, Ar-H], 7.07 ppm [s, 2H, Ar-H], 7.13 ppm [s, 2H, Ar-H], 7.93 ppm [dd, 4H, C**H**CN], 8.45 ppm [dd, 4H, C**H**CHCN], 8.81 ppm [dd, 2H, C**H**N] |
| **UV-Vis ($CH_2Cl_2$)** | $\lambda_{max}$/nm = 327, 399 Concentration: $2e^{-6}$ mol/L |
| **Fluorescence** | $\lambda_{max}$ (Excitation) = 343.91 nm, 353.67 nm, 393.23 nm<br>$\lambda_{max}$ (Emission) = 457.04 nm |
| **MALDI-TOF (CHCA Matrix)** | (Pulse Voltage: 2009 V, MCP Voltage: 2350 V) m/z (rel. int. %) 1394.1 (100) $[M+1]^{+\bullet}$ |

### 4.1.34 Preparation of Polymer - (39)

To a 100 ml oven-dried Schlenk flask was added Monomer **38** (100 mg, 0.072 mmol) in 12 ml of dry toluene and 5 ml diisopropylamine. The solution was degassed for 1 hr. 1,3-bis(4-ethynphenoxy)propane **10** (20 mg, 0.072 mmol) was then added followed by $Pd(PPh_3)_4$ (4 mg, 0.0031 mmol, 5 mol %) and CuI (1 mg, 0.0031 mmol, 5 mol %). The reaction was allowed to proceed at 80 ºC for four days. The mixture was then transferred to a separatory funnel via the addition of 30 ml of toluene and extracted with water three times. The organic layer was then dried over magnesium sulfate. The light orange solution was concentrated and added drop-wise to a vigorously stirred and cooled solution of methanol. The precipitate was collected and washed repeatedly with methanol to yield bright orange crystals. These crystals were subjected to a Soxhlett extraction with methanol for three days.

**Yield** ( 66 %)

**$^1$H NMR** (400 MHz, $CDCl_3$, 25 °C): δ = 0.89 ppm [m, 18 H, C**H$_3$**], 1.55 ppm [m, 48H, C**H$_2$**], 2.29 ppm [q, 2H, $OCH_2C$**H$_2$**$CH_2$], 4.02 ppm [m, 8H, OC**H$_2$** end units], 4.08 ppm [m, 4H, OC**H$_2$** center unit],
4.17 ppm [m, 4H, OC**H$_2$**$CH_2C$**H$_2$**O], 6.88 ppm [m, 4H, Ar-H (C3 spacer)], 7.04 ppm [s, 2H, Ar-H], 7.07 ppm [s, 2H, Ar-H], 7.13 ppm [s, 2H, Ar-H], 7.46 ppm [m, 4H, Ar-H (C3 spacer)], 7.93 ppm [d, 2H, Bipyr-H], 8.43 ppm [d, 2H, Bipyr-H], 8.82 ppm [d, 2H, Bipyr-H]

**$^{13}$C {$^1$H} NMR** (400 MHz, $CDCl_3$, 25 °C): δ = 14.04 ppm, 14.06 ppm, 22.66 ppm, 25.75 ppm, 29.15 ppm, 29.27 ppm, 31.52 ppm, 31.62 ppm, 64.35 ppm, 69.64 ppm, 69.83 ppm, 70.18 ppm, 81.23 ppm, 89.98 ppm, 111.80 ppm, 113.85 ppm, 114.18 ppm, 114.53 ppm, 114.64 ppm, 116.78 ppm, 117.51 ppm, 117.95 ppm, 117.96 ppm, 120.62 ppm, 133.12 ppm, 134.07 ppm, 139.20 ppm, 139.25 ppm, 149.52 ppm, 151.65 ppm, 151.71 ppm, 153.81 ppm, 154.08 ppm, 154.17 ppm, 154.34 ppm

**UV-VIS ($CH_2Cl_2$)** $\lambda_{max}$/nm = 282, 327, 344, 403 Concentration: $8e^{-6}$ mol/L

**GPC (THF)** $M_n$: 9,983 g/mol, $M_w$: 129,963 g/mol
polydispersity index = 13.02

**Fluorescence** $\lambda_{max}$ (Excitation) = 395.24 nm
$\lambda_{max}$ (Emission) = 458.18 nm

### 4.1.35 Preparation of Polymer - (44)

Monomer **21** (0.2662 g, 0.21 mmol), 1,2-bis(4-ethynphenoxy)ethane **7** (0.0558 g, 0.21 mmol), $Pd(PPh_3)_4$ (9.82 mg, 0.0085 mmol, 4 mol %), and CuI (2.50 mg, 0.0085 mmol, 4 mol %) were added to a degassed solution of 10 ml diisopropylamine and 40 ml toluene in a 250 ml round-bottom schlenk flask. After degassing the reaction mixture for a further 1 hr, it was stirred at 70-75 °C. After a total reaction time of 96 h, 10 ml of toluene was added and the reaction mixture was transferred to a 250 ml separatory funnel. The mixture was then extracted three times with 60 ml portions of water. The organic layer was then dried over magnesium sulfate. The light orange solution was concentrated and added drop-wise to a vigorously stirred and cooled solution of methanol. The precipitate was collected and washed repeatedly with methanol to yield bright orange crystals. These crystals were subjected to a Soxhlett extraction with methanol for three days.

**Yield** ( 86 % )

**$^1$H NMR** (400 MHz, $CDCl_3$, 25 °C): δ = 0.87 ppm [m, 12H, C**H$_3$**], 1.52 ppm [m, 80H, C**H$_2$**], 4.01 ppm [m, 8H, OC**H$_2$**], 4.35 ppm [t, 4H, OC**H$_2$**C**H$_2$**], 6.92 ppm [m, 4H, Ar-H (C2 spacer)], 7.03 ppm [s, 2H, Ar-H], 7.13 ppm [s, 2H, Ar-H], 7.48 ppm [m, 4H, Ar-H (C2 spacer)], 7.92 ppm [dd, 2H, Bipyr-H], 8.43 ppm [dd, 2H, Bipyr-H], 8.81 ppm [dd, 2H, Bipyr-H]

**$^{13}$C {$^1$H} NMR** (400 MHz, $CDCl_3$, 25 °C): δ = 14.12 ppm, 22.70 ppm, 26.01 ppm, 26.03 ppm, 29.19 ppm, 29.22 ppm, 29.31 ppm, 29.35 ppm, 29.42 ppm, 29.45 ppm, 29.55 ppm, 29.57 ppm, 29.58 ppm, 29.61 ppm, 29.65 ppm,

| | |
|---|---|
| | 29.71 ppm, 29.72 ppm, 31.91 ppm, 31.93 ppm, 69.86 ppm, 70.18 ppm, 89.95 ppm, 90.94 ppm, 111.84 ppm, 114.16 ppm, 114.69 ppm, 114.81 ppm, 117.50 ppm, 117.99 ppm, 120.57 ppm, 120.68 ppm, 133.15 ppm, 134.11 ppm, 139.15 ppm, 149.52 ppm, 151.64 ppm, 153.49 ppm, 154.09 ppm, 154.34 ppm |
| **UV-Vis** | $\lambda_{max}$/nm = 284, 327, 345, 380 Concentration: $1e^{-5}$ mol/L |
| **($CH_2Cl_2$)** | |
| **Elemental** | C (81.73 %), H (9.10 %), N (2.07 %), = Calculated |
| **Analysis** | C (78.48 %), H (8.41 %), N (2.05 %) = Actual |
| **GPC (THF)** | $M_n$: 7,099 g/mol, $M_w$: 14,486 g/mol |
| | Polydispersity index = 2.04 |
| **Fluorescence** | $\lambda_{max}$ (Excitation) = 388.01 nm |
| | $\lambda_{max}$ (Emission) = 468.25 nm |

### 4.1.36 Preparation of Polymer - (45)

Monomer **21** (0.2662 g, 0.21 mmol), 1,3-Bis(4-ethynphenoxy)propane **10** (0.0589 g, 0.21 mmol), $Pd(PPh_3)_4$ (9.90 mg, 0.0085 mmol, 4 mol %), and CuI (2.5 mg, 0.0085 mmol, 4 mol %) were added to a degassed solution of 10 ml diisopropylamine and 40 ml toluene in a 250 ml round-bottom schlenk flask. After degassing the reaction mixture for a further 1 hr, it was stirred at 70-75 °C. After a total reaction time of 96 h, 10 ml of toluene was added and the reaction mixture was transferred to a 250 ml separatory funnel. The mixture was then extracted three times with 60 ml portions of water. The organic layer was then dried over magnesium sulfate. The light orange solution was concentrated and added drop-wise to a vigorously stirred and cooled solution of methanol. The precipitate was collected and washed repeatedly with methanol to yield bright orange crystals. These crystals were subjected to a Soxhlett extraction with methanol for three days.

**Yield** (88 %)

**$^1$H NMR** (400 MHz, $CDCl_3$, 25 °C): δ = 0.86 ppm [m, 12H, C**H$_3$**], 1.53 ppm [m, 80H, C**H$_2$**], 2.28 ppm [q, 2H, $OCH_2C$**H$_2$**$CH_2$], 4.01 ppm [m, 8H, OC**H$_2$**], 4.17 ppm [q, 4H, OC**H$_2$**$CH_2C$**H$_2$**O], 6.87 ppm [m, 4H, Ar-H (C3 spacer)], 7.03 ppm [s, 2H, Ar-H], 7.13 ppm [s, 2H, Ar-H], 7.46 ppm [m, 4H, Ar-H (C3 spacer)], 7.92 ppm [dd, 2H, Bipyr-H], 8.43 ppm [dd, 2H, Bipyr-H], 8.81 ppm [dd, 2H, Bipyr-H]

**$^{13}$C {$^1$H} NMR** (400 MHz, $CDCl_3$, 25 °C): δ = 14.13 ppm, 22.70 ppm, 26.00 ppm, 26.03 ppm, 29.19 ppm, 29.24 ppm, 29.33 ppm, 29.37 ppm, 29.41 ppm, 29.45 ppm, 29.58 ppm, 29.59 ppm, 29.61 ppm, 29.64 ppm, 29.66 ppm, 29.69 ppm, 29.71 ppm, 29.72 ppm, 31.92 ppm, 31.94 ppm, 69.86 ppm, 70.19 ppm, 89.95 ppm, 90.94 ppm, 111.84 ppm, 114.16 ppm, 114.53 ppm, 114.64 ppm, 117.50 ppm, 117.99 ppm, 120.57 ppm, 120.68 ppm, 133.13 ppm, 134.07 ppm, 139.16 ppm, 149.52 ppm, 151.65 ppm, 154.09 ppm, 154.34 ppm

**UV-Vis ($CH_2Cl_2$)** $\lambda_{max}$/nm = 284, 323, 345, 382 Concentration: $1.2e^{-5}$ mol/L

**Elemental Analysis** C (81.77 %), H (9.15 %), N (2.05 %), = Calculated
C (79.52 %), H (8.27 %), N (2.03 %) = Actual

**GPC (THF)** $M_n$: 7,268 g/mol, $M_w$: 14,468 g/mol
Polydispersity index = 1.99

**Fluorescence** $\lambda_{max}$ (Excitation) = 388.32 nm
$\lambda_{max}$ (Emission) = 469.47 nm

### 4.1.37 Isolation of Monomer - (46)

**Yield** ( 45 % )

**$^1$H NMR** (250 MHz, $CDCl_3$, 25 °C): δ = 0.86 ppm [q, 18 H, C**H$_3$**], 1.54 ppm [m, 120 H, C**H$_2$**], 4.00 ppm [t, 8H, OC**H$_2$** (end units)], 4.01 ppm [t, 4H, OC**H$_2$** (center unit)], 7.04 ppm [s, 2H, Ar-H], 7.07 ppm [s, 2H, Ar-H],

| | |
|---|---|
| | 7.13 ppm [s, 2H, Ar-H], 7.93 ppm [d, 4H, C**H**CN], 8.44 ppm [d, 4H, C**H**CHCN], 8.82 ppm [d, 4H, C**H**N] |
| **$^{13}$C {$^{1}$H} NMR** | (250 MHz, $CDCl_3$, 25 °C): δ = 14.34 ppm, 22.92 ppm, 26.21 ppm, 26.25 ppm, 26.30 ppm, 29.42 ppm, 29.46 ppm, 29.53 ppm, 29.56 ppm, 29.59 ppm, 29.63 ppm, 29.80 ppm, 29.82 ppm, 29.89 ppm, 29.90 ppm, 29.92 ppm, 32.14 ppm, 32.15 ppm, 69.88 ppm, 70.07 ppm, 70.40 ppm, 90.21 ppm, 90.64 ppm, 91.16 ppm, 92.35 ppm, 94.08 ppm, 107.50 ppm, 112.03 ppm, 114.09 ppm, 114.40 ppm, 117.03 ppm, 117.21 ppm, 117.72 ppm, 118.20 ppm, 120.83 ppm, 139.42, 149.74 ppm, 151.93 ppm, 154.04 ppm, 154.35 ppm, 154.57 ppm |
| **UV-VIS ($CH_2Cl_2$)** | $\lambda_{max}$/nm = 284, 348, 399 Concentration: $8e^{-6}$ mol/L |
| **Elemental Analysis** | C (74.66 %), H (8.92 %), N (2.95 %), = Calculated<br>C (71.88 %), H (8.87 %), N (2.88 %) = Actual |
| **MALDI-TOF (CHCA Matrix)** | (Pulse Voltage: 2009 V, MCP Voltage: 2350 V) m/z (rel. int. %) 1899.10 (100) $[M+1]^{+\bullet}$ |

### 4.1.38 Preparation of Polymer - (47)

Monomer **46** (0.040 g, 0.021 mmol), 1,3-Bis(4-ethynphenoxy)propane **10** (0.006 g, 0.021 mmol), $Pd(PPh_3)_4$ (4 mg, 0.0032 mmol, 16 mol %), and CuI (2 mg, 0.0032 mmol, 16 mol %) were added to a degassed solution of 10 ml diisopropylamine and 20 ml toluene in a 50 ml screw-cap schlenk vessel. After degassing the reaction mixture for a further 1 hr, it was stirred at 80 °C. After a total reaction time of 96 h, 10 ml of toluene was added and the reaction mixture was transferred to a 250 ml separatory funnel. The mixture was then extracted three times with 60 ml portions of water. The organic layer was then dried over magnesium sulfate. The light orange solution was concentrated and added drop-wise to a vigorously stirred and cooled solution of methanol. The precipitate was collected and washed repeatedly with

methanol to yield bright orange crystals. These crystals were subjected to a Soxhlett extraction with methanol for three days.

| | |
|---|---|
| **Yield** | ( 68 %) |
| **$^1$H NMR** | (400 MHz, $CDCl_3$, 25 °C): δ = see figure 11, Chapter 3.3.2 |
| **UV-Vis ($CH_2Cl_2$)** | $\lambda_{max}$/nm = 327, 345, 397 Concentration: $6e^{-6}$ mol/L |
| **Elemental Analysis** | C (81.75 %), H (9.11 %), N (2.78 %), = Calculated<br>C (75.20 %), H (8.60 %), N (2.54 %) = Actual |
| **GPC (THF)** | $M_n$: 6,475 g/mol, $M_w$: 10,839 g/mol<br>polydispersity index = 1.67 |
| **Fluorescence** | $\lambda_{max}$ (Excitation) = 393 nm<br>$\lambda_{max}$ (Emission) = 455 nm |

## 5. Thesis Summary

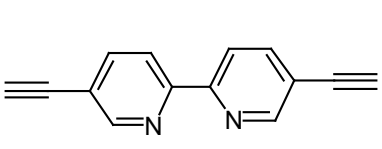
Π-conjugated polymers, typified by polyphenylene (PPP), polyphenylene vinylene (PPV), and polyphenylene ethynylene (PPE), represent a class of organic-based materials that possess unique optical and electronic properties, including high electronic conductivity in the doped polymers, high absorptivity in the visible and/or near IR regions, and large fluorescence quantum yields.

The electronic properties of such conjugated macromolecules are primarily governed by the chemical structure of the polymer backbone itself, however, a number of additional tools can be employed in order to further manipulate the bandgap of conjugated polymers. Control of the effective conjugation length by the introduction of side chains which exhibit steric interactions and force the backbone to twist, along with the design of copolymers that comprise well-defined conjugated segments, are illustrative examples of how emission color can be varied over a broad spectrum. In the case of PPV, shortening of the effective conjugation length is essential in order to shift the emission spectrum from green to blue. In addition, the improvement of electroluminescence can be achieved by the introduction of non-conjugated segments in the main chains.

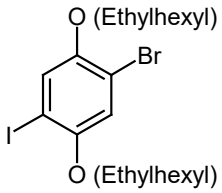
The principle objective of this work was to synthesize new PAE's containing both conjugated rigid units and flexible non-conjugated units. The alternating block copolymers were designed so that one could study the effect on opto-electronic properties of having both conjugated, rigid bipyridine-based aromatic units and non-conjugated, flexible alkyl diether units in the main polymeric chain. The length of the conjugated moieties in the polymer backbone, the length of the non-conjugated moieties in the polymer backbone, and finally the length of the side chains were varied, and the effects of their variation on the polymers opto-electronic properties were investigated.

The following thesis summary documents the results of this work:

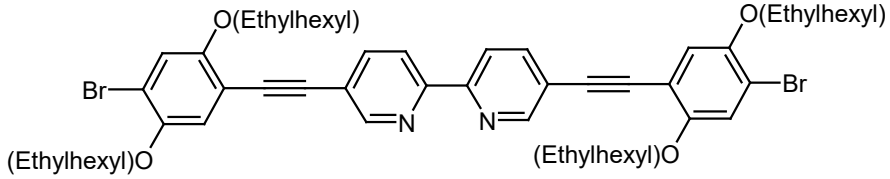
1) The synthesis of monomer **14** began with the synthesis of 5,5'-diethynyl-2,2-bipyridne (**4)** and the iodo-bromo compound **13.** Using the Sonogashira Pd-cross coupling reaction, monomer **14** was synthesized in high purity.




**4**

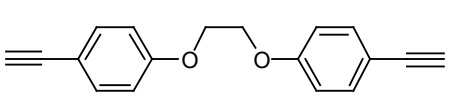



**13**

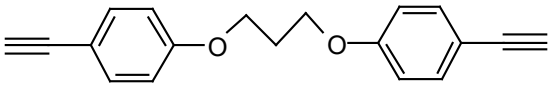



**14**

2) The second type of monomer (**7 & 10)**, the non-conjugated spacers, were synthesized from the corresponding dibromo compounds and 2-methyl-3-butyn-2-ol (MBI), in moderate yields and high purity.

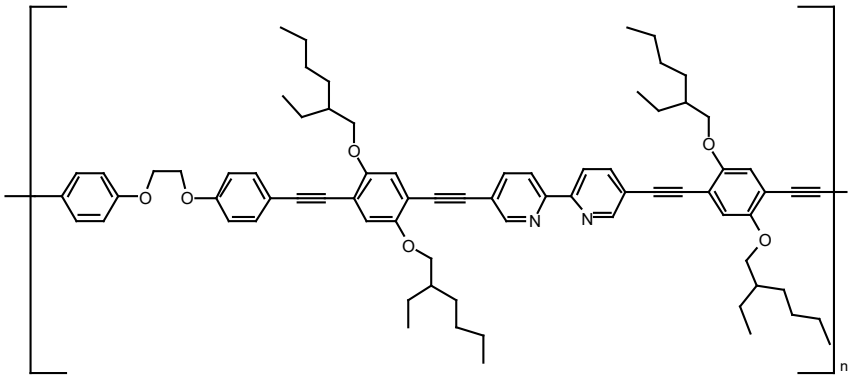



**7**

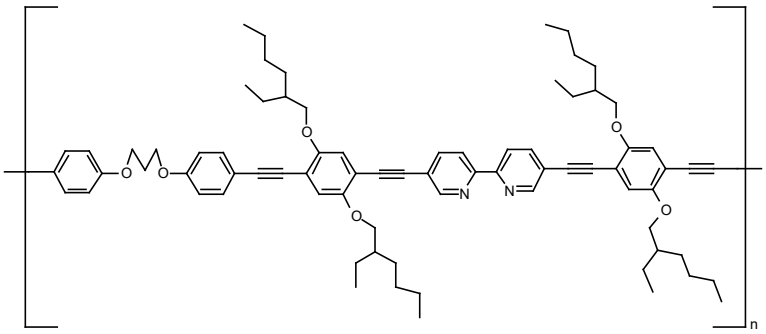



**10**

3) The Sonogashira Pd-cross coupling reaction of monomer **14** with monomers **7** and **10**, in toluene, yields polymers **15** and **36**, respectively. The molecular weights of both polymers were determined by GPC and found to be $M_n$ = 8,736 g/mol ( polydispersity index 1.77) for polymer **15** and $M_n$ = 12,005 g/mol for polymer **36** (polydispersity index 1.78).

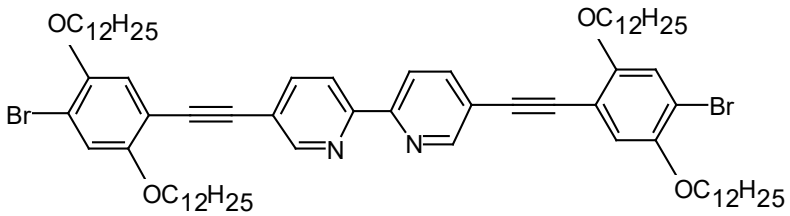


**15**



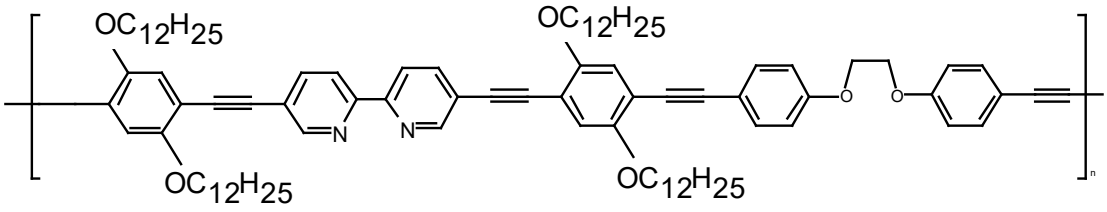
**36**

4) The absorption maxima ($\lambda_{max}$ = 400 nm) of polymer **15** was found to be 10 nm bathochromically shifted compared to polymer **36** with the longer aliphatic spacer. The same trend was observed in the fluorescence emission maxima of both polymers ($E_{max}$ = 485 nm for polymer **15** and $E_{max}$ = 479 nm for polymer **36**).
5) To investigate the effect of the side chain length on the polymer properties, another dibromo-monomer **21** with $C_{12}$ side chains was synthesized. The synthetic methodology selected for this compound was analogous to that of monomer **14**.

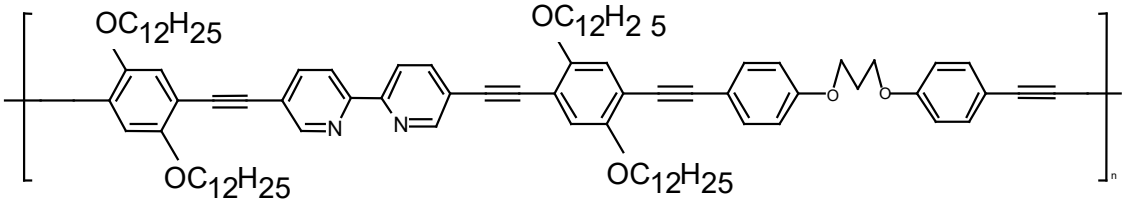


**21**

6) Polymers **44** and **45** were synthesized using Sonogashira Pd-cross coupling reactions of monomer **21** with monomers **7** and **10**, respectively. The molecular weights of the subsequent polymers were determined by GPC to be 7,100 g/mol for polymer **44** (polydispersity index 2.04) and 7,300 g/mol for polymer **55** (polydispersity index 1.99).

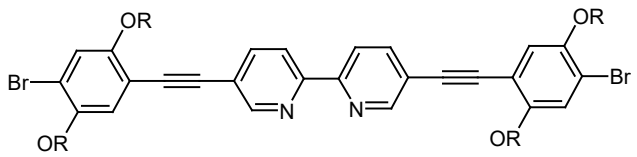



**44**



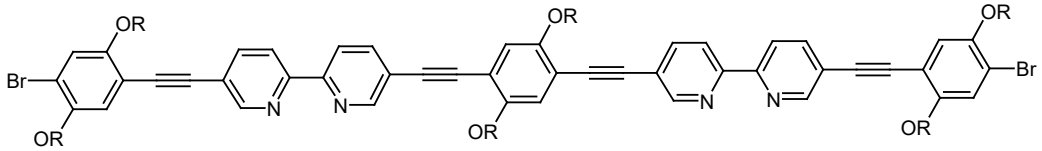

**45**

7) The absorption maxima of these polymers were determined by UV-Vis spectroscopy and compared to those of polymers **15** and **36,** with shorter alkyl side chains. It was found that the $\lambda_{max}$ for polymers **44** and **45** are virtually the same at 380 nm and 382 nm, respectively. However, it was found that the introduction of longer aliphatic chains into the side chains of the polymers shifts the $\lambda_{max}$ in the UV hypsochromically by about 11-20 nm. The fluorescence spectra of both polymers were determined in methylene chloride and found to be similar at $E_{max}$ = 468 nm. Comparing these values to the values obtained for polymers **15** and **36**, having shorter and branched aliphatic side chains, reveals that the $E_{max}$ for these polymers are hypsochromically shifted, following the same trend found in the absorption maxima.
8) During the synthesis of the dibromo monomers **14**, **21**, and **27**, the formation of side products with relatively high yields (40-45 %) was observed. Further NMR and MALDI-TOF mass spectroscopy analyses revealed the presence of the extended monomers **38** and **46**.




R = $C_6H_{13}$ **(27)**

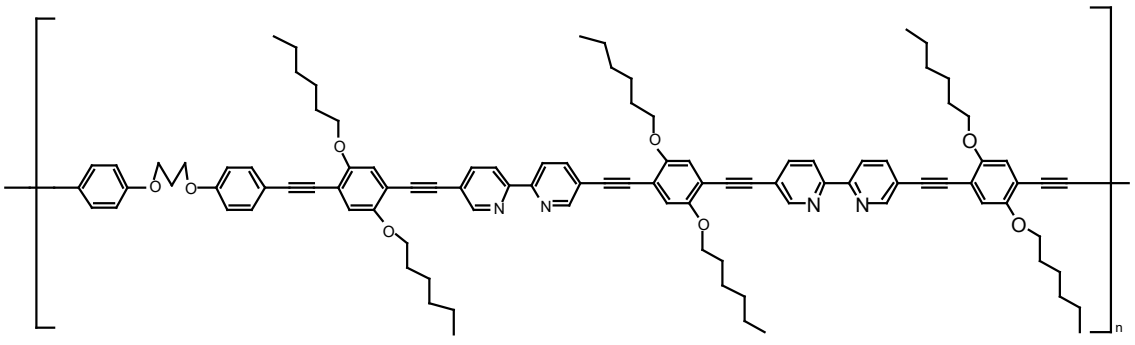
R= $C_{12}H_{25}$ **(21)**



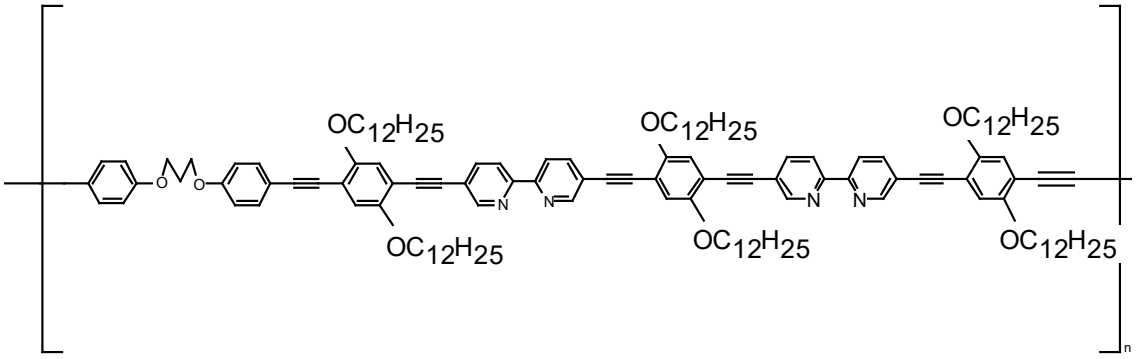

R = $C_6H_{13}$ **(38)**

R = $C_{12}H_{25}$ **(46)**

9) Since one of the main objectives of this work was to study the effect of the length of the rigid conjugated moiety of the polymer backbone on optical properties, monomer **38** and monomer **46** were reacted with the diacetylene compound **10** using Sonogashira Pd-cross coupling protocols. The molecular weights of the polymers were found to be $M_n$ = 9,983 g/mol for polymer **39** and $M_n$ = 6,470 g/mol for polymer **47**.



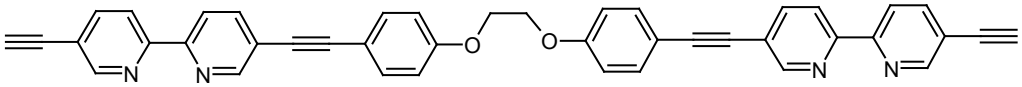

**39**



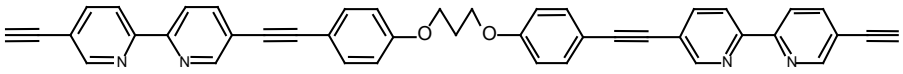
**47**

10) The absorption maxima of both polymers **39** and **47** were found to be very close at 403 nm and 397 nm, respectively. As expected, the absorption maxima of these polymers, with extended conjugated units, is bathochromically shifted compared to polymers **36** and **45** with shorter conjugation. However, the emission maxima $E_{max}$ of the extended polymers **39** and **47** were found to be slightly hypsochromically shifted compared to the polymers with shorter conjugated segments. It was found that the values of the Stokes' shifts of extended polymers **39** and **47** are lower (63 and 62) compared to polymers **36** and **45** at 88 and 81, respectively.

11) The final polymer, exhibiting the longest conjugated moiety, was arrived at via the development of monomers **34** and **34-B.** The dihydroxy precursor (**33**) of compound **34** was found to be insoluble in organic solvents and the conversion to final monomer **34** was not accomplished. Therefore, compound **34-B** was synthesized. The structures of both monomers were confirmed by NMR-spectroscopy and MALDI-TOF mass spectroscopy.

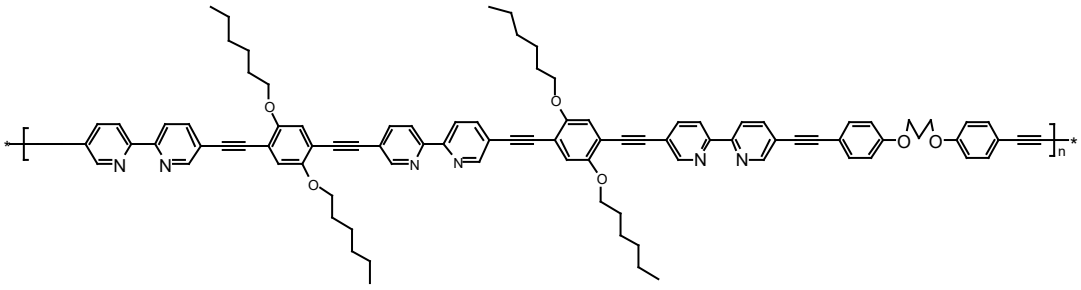


**34**



**34-B**

12) The Sonogashira Pd-cross coupling reaction of compound **34-B** with the dibromo monomer **27** was carried out in toluene to produce polymer **35-B**, having three bipyridine units in the monomer unit.



**35-B**

13) The molecular weight of polymer **35-B** was found to be $M_n$ = 5,200 g/mol. The polydispersity index was determined at 1.34. The UV-Vis spectrum of this polymer showed an absorption maximum at 381 nm. The emission maximum $E_{max}$ of the polymer was determined in methylene chloride and found to be at 460 nm.

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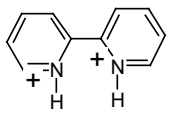
# 7. Appendix

## 7.1 List of Compounds Synthesized



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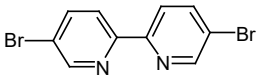

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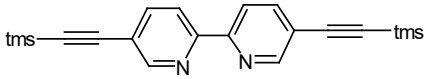

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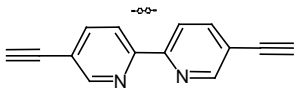

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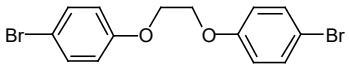

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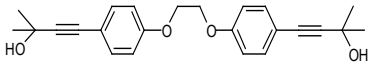

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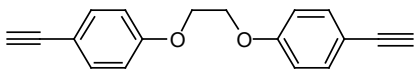

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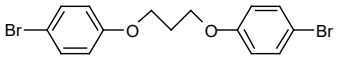

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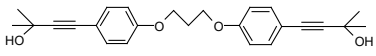

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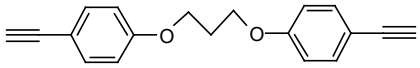

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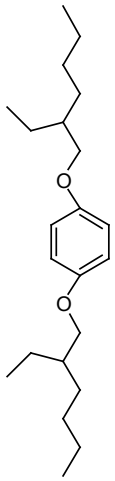

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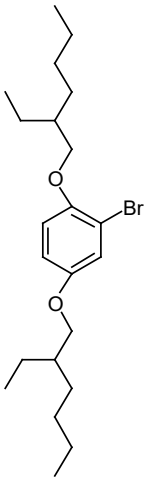

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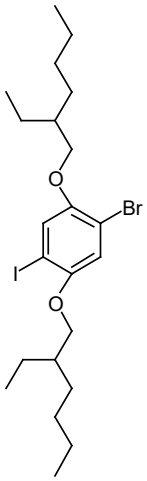

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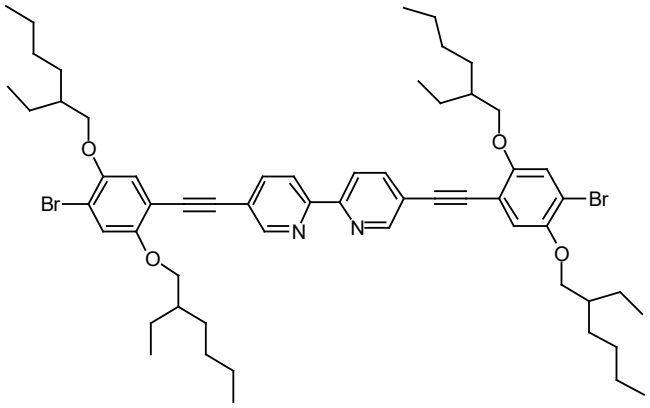


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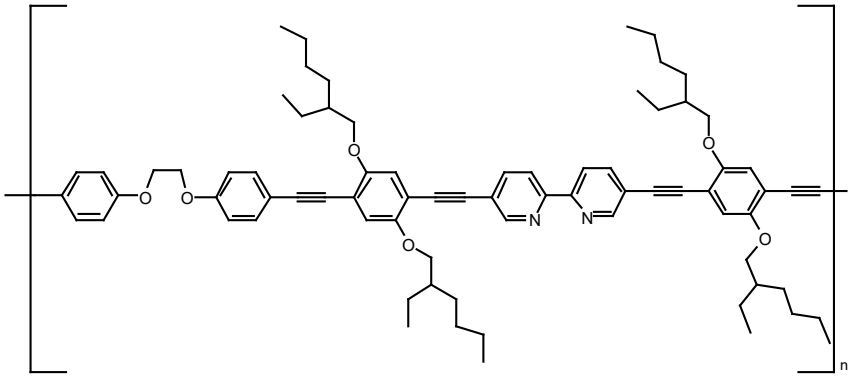


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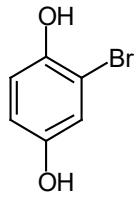


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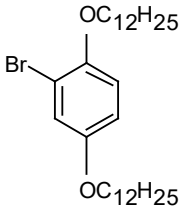


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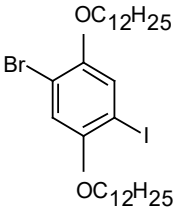


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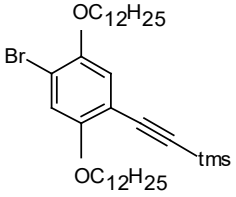


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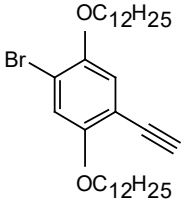


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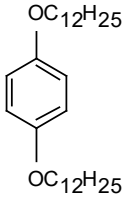


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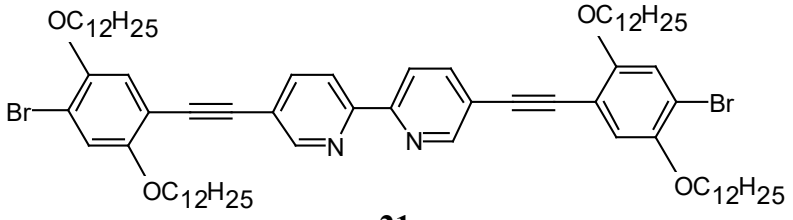


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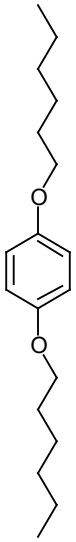


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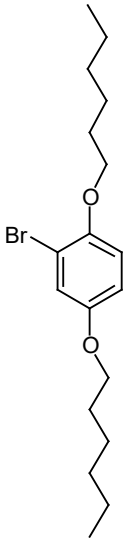


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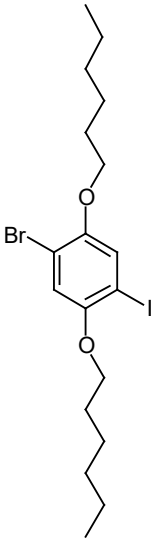


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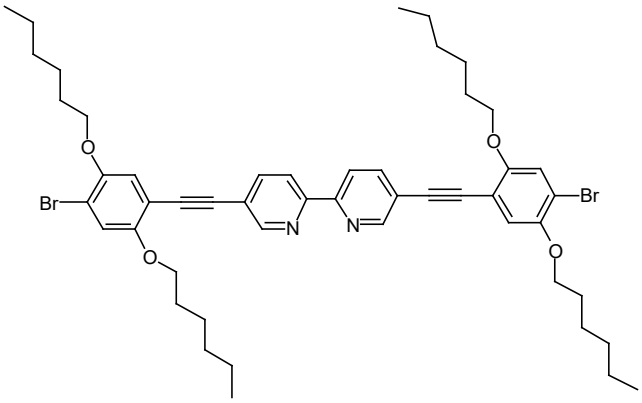


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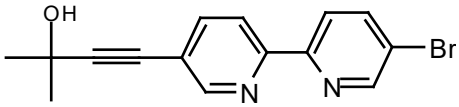


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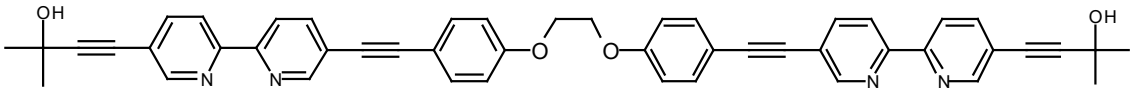

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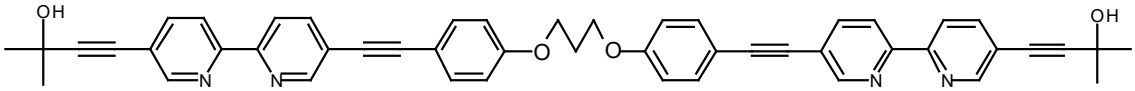

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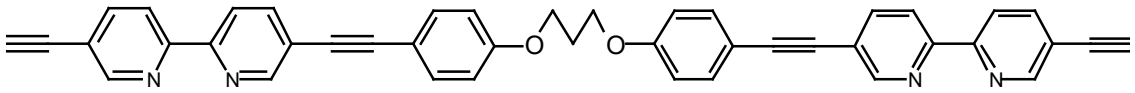

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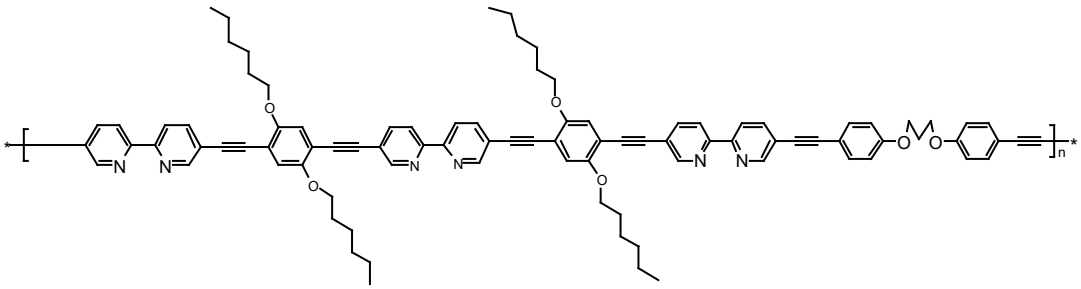

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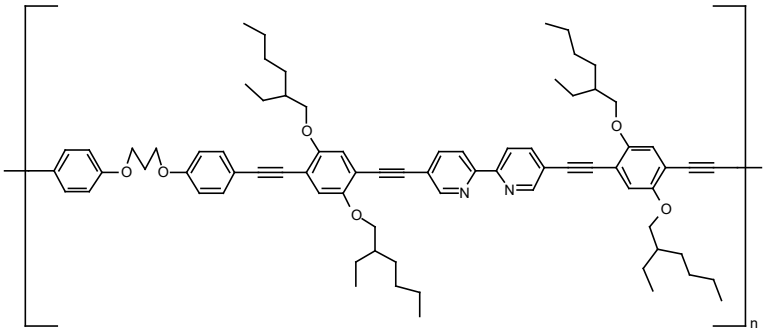

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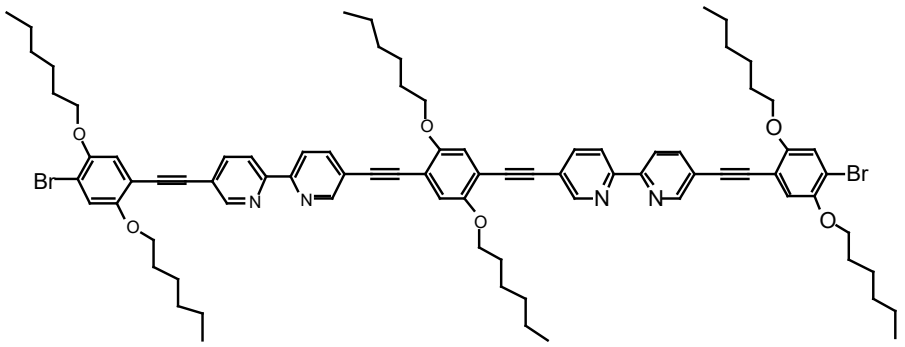

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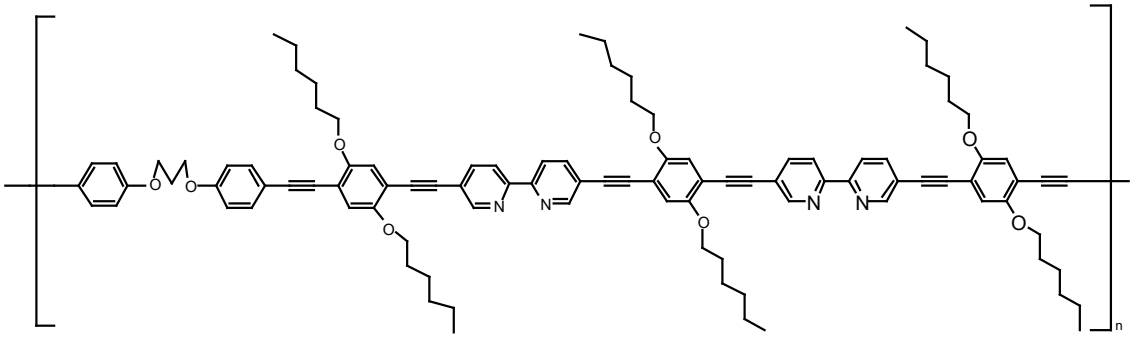

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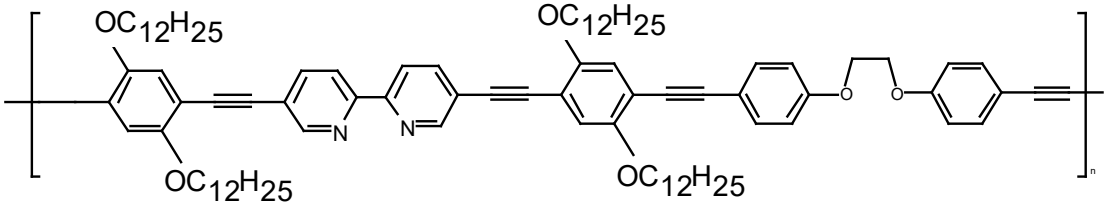

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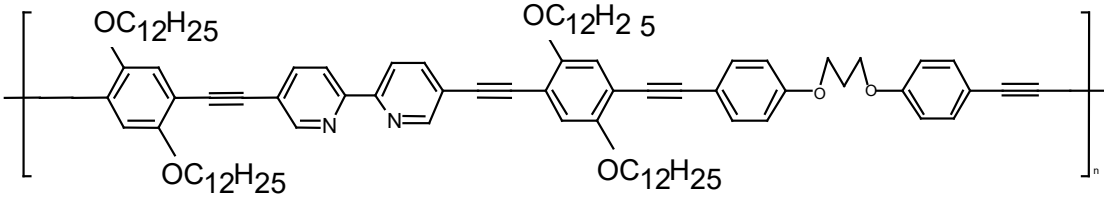

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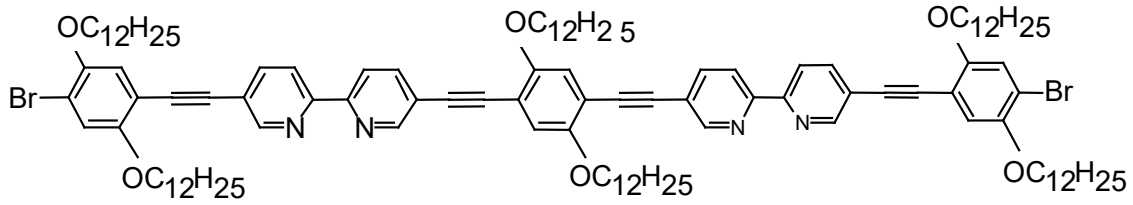
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OC12H25
OC12H25

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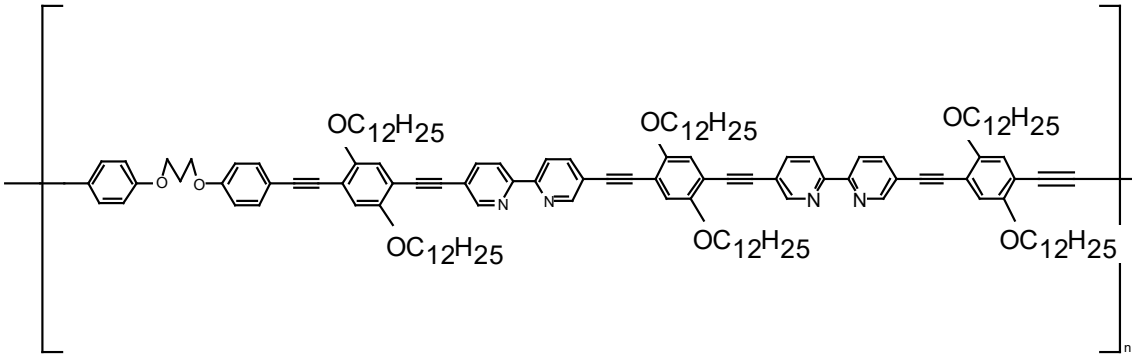
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N
N
N
N
OC12H25
OC12H25
OC12H25
n

**47**

## 7.2 Abbreviations

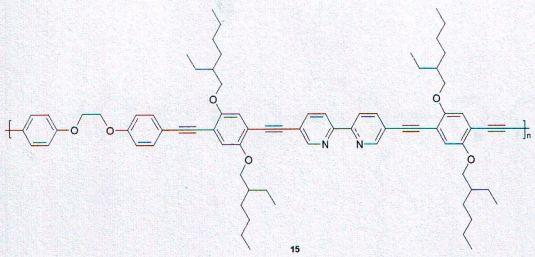
| | |
|---|---|
| Ar | Aryl group |
| br | Broad |
| *c* | Path length |
| $cm^3$ | Centimeter cubed |
| $cm^{-1}$ | Centimeter inverse |
| $CDCl_3$ | Deuterated chloroform |
| $CHCl_3$ | Chloroform |
| CuI | Copper (I) Iodide |
| δ | Delta (chemical shift) |
| d | Day or doublet (NMR) |
| d of tr | Doublet of triplets (NMR) |
| dd | Doublet of doublets (NMR) |
| DMF | Dimethyl Formamide |
| DMSO | Dimethyl Sulfoxide |
| ε | Molar Absorption Coefficient |
| eq | Equivalents |
| eV | Electron Volt |
| EI-MS | Electron impact mass spectrum |
| g | Gram |
| GPC | Gel Permeation Chromatography |
| h | Hour |
| IR | Infrared |
| L | Liter |
| LED | Light-emitting Diode |
| $\lambda_{max}$ | Lambda (at maximum absorption) |
| m | Multiplet |
| M | Molarity (mol/L) |
| mg | Milligram |
| MHz | Megahertz |
| min | Minutes |
| ml | Milliliter |
| mmol | Millimole |
| mol | Mole |
| mp | Melting Point |
| $M_n$ | Number Average Molecular Weight |
| $M_w$ | Weight Average Molecular Weight |
| m/z | Mass to Charge |
| n | Number of Monomer Units in Polymer |
| NMR | Nuclear Magnetic Resonance |
| OR | Alkoxy group |
| OLED | Organic Light Emitting Diode |
| ppm | Parts per Million |
| PAE | Polyarylethynylene |

| | |
|---|---|
| PPE | Polyphenyleneethynylene |
| PPV | Polyphenylvinylene |
| q | Quintet (NMR) |
| qr | Quartet (NMR) |
| rt | Room temperature |
| s | Singlet |
| *tert* | Tertiary |
| THF | Tetrahydrofuran |
| TMS | Tetramethylsilane |
| tr | Triplet |
| UV/Vis | Ultra-violet/Visible Spectroscopy |

## 7.3 List of Figures

## 7.4 List of Schemes

## 7.5 $^{13}$C-NMR Spectra



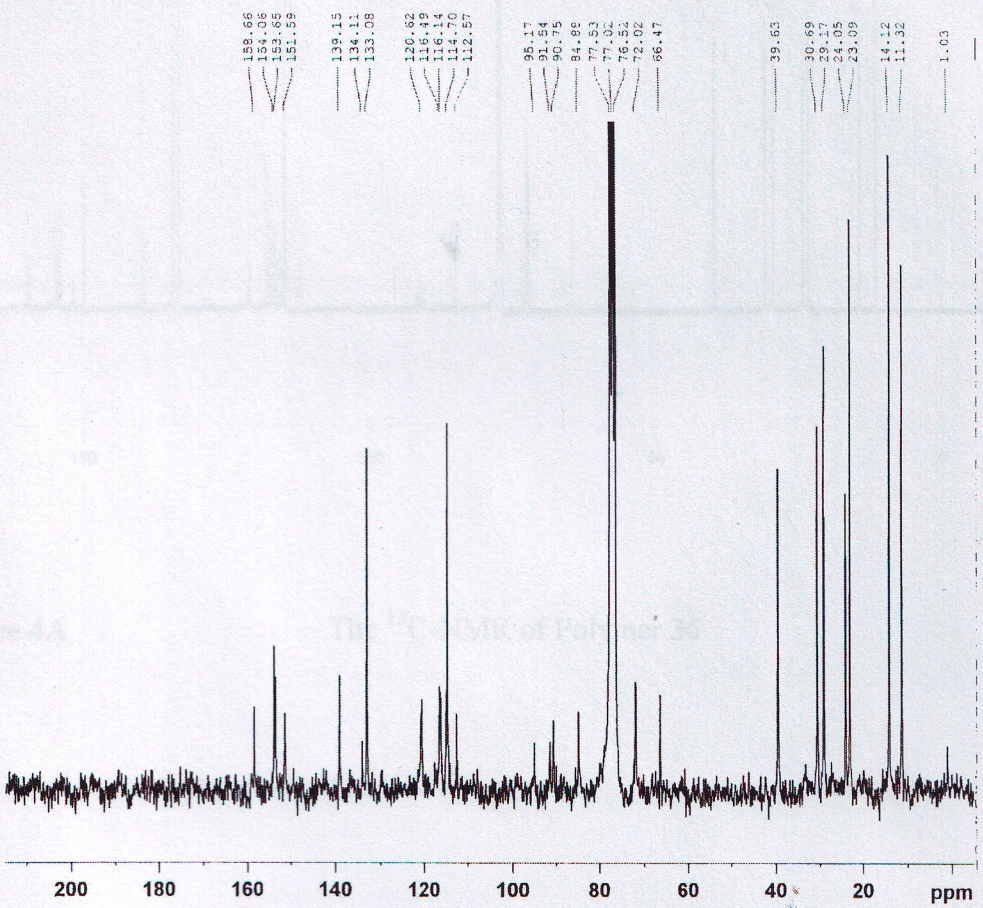



**Figure 2A** The $^{13}$C-NMR of Polymer **15**

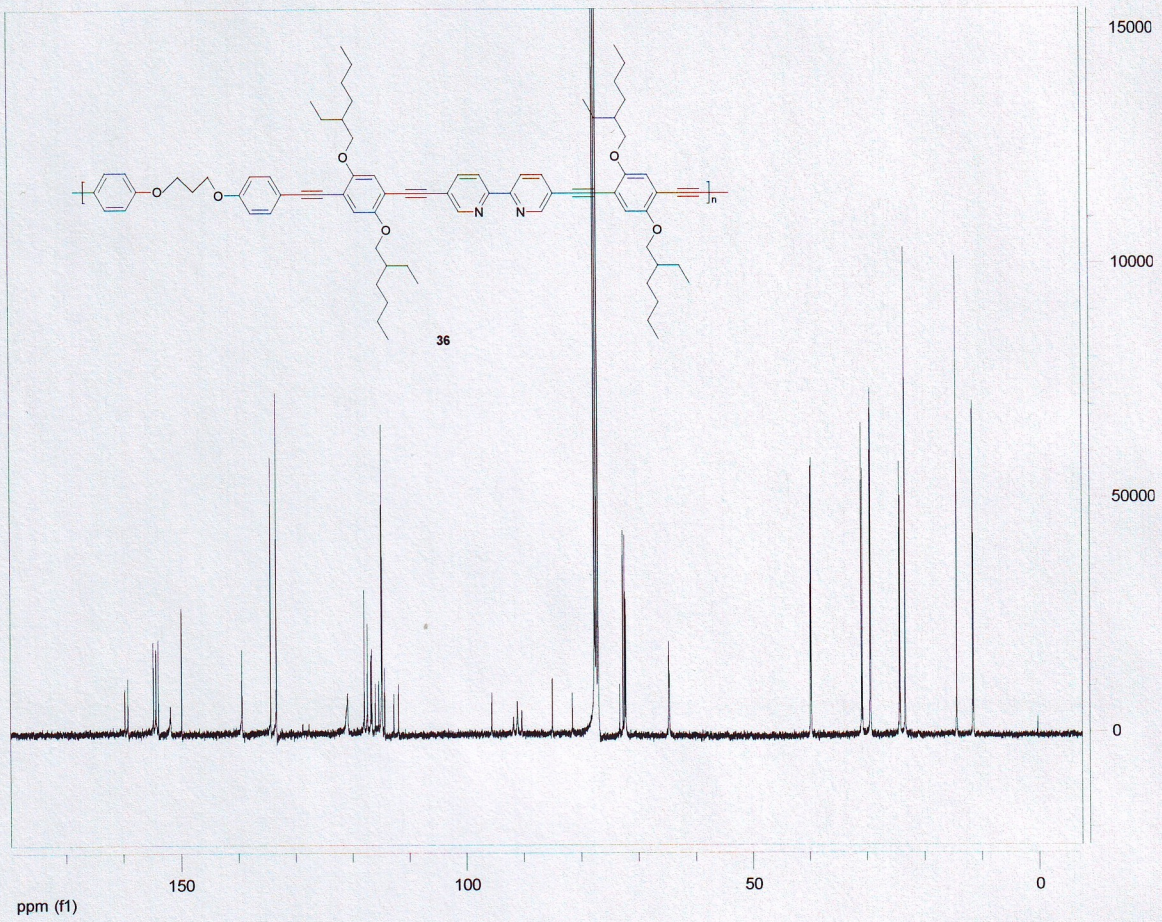



**Figure 4A** The $^{13}$C-NMR of Polymer **36**

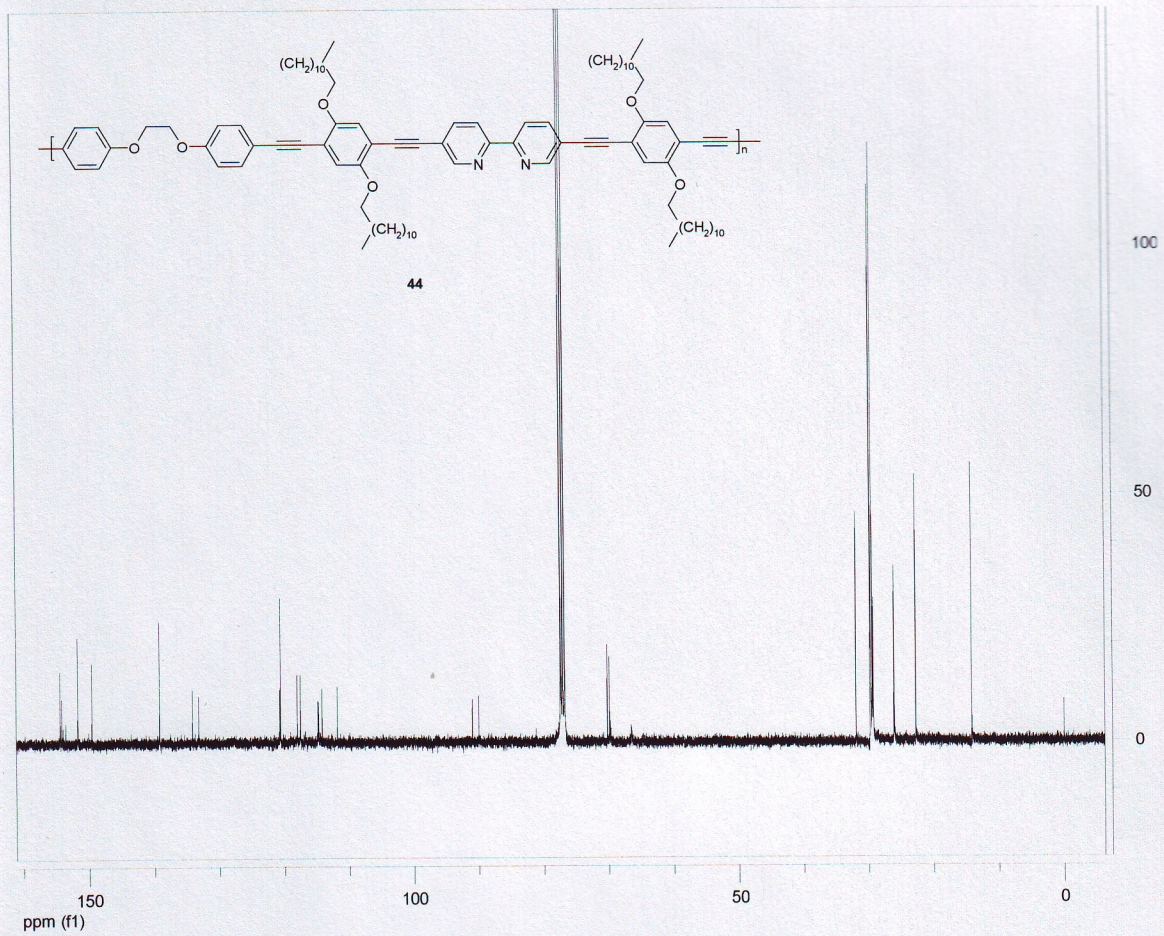



**Figure 6A** The $^{13}$C-NMR of Polymer **44**

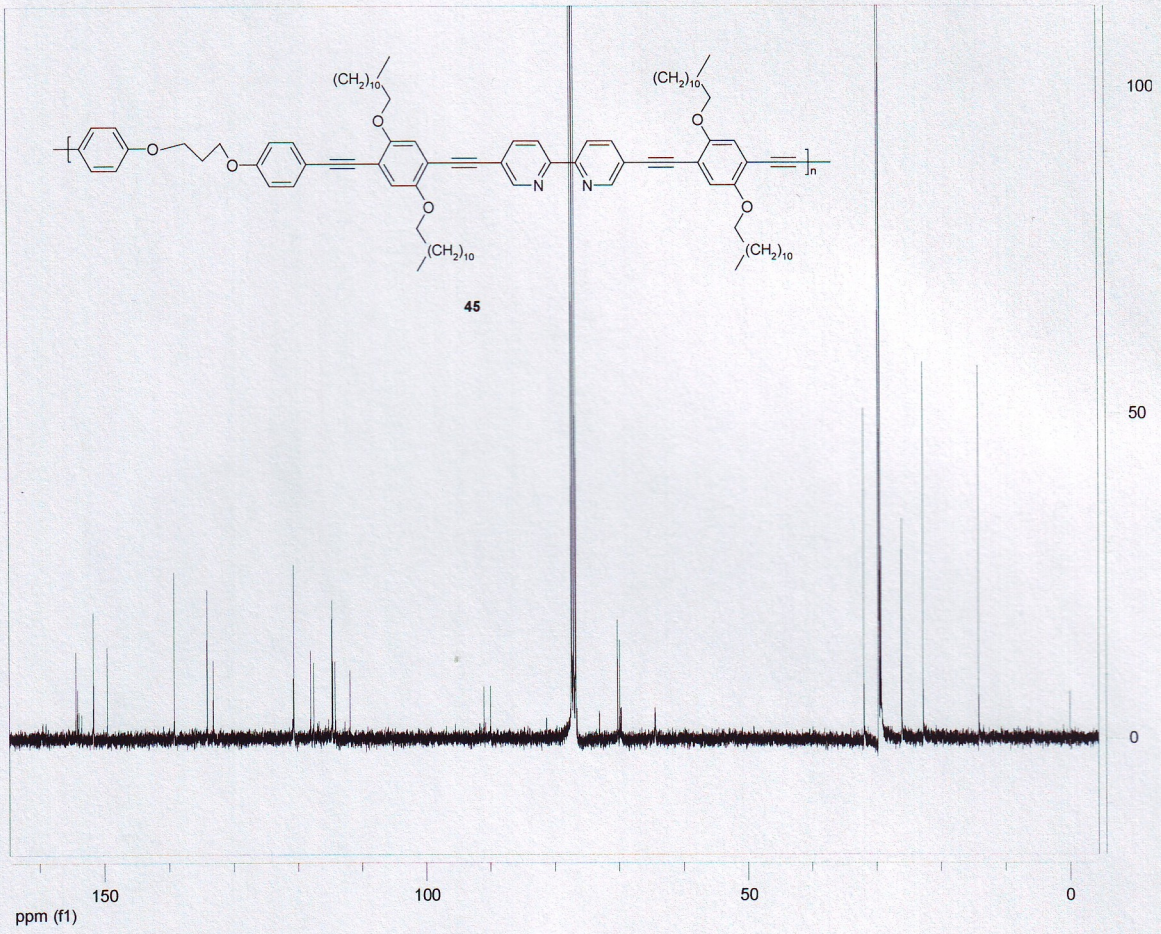



**Figure 7A** The $^{13}$C-NMR of Polymer **45**

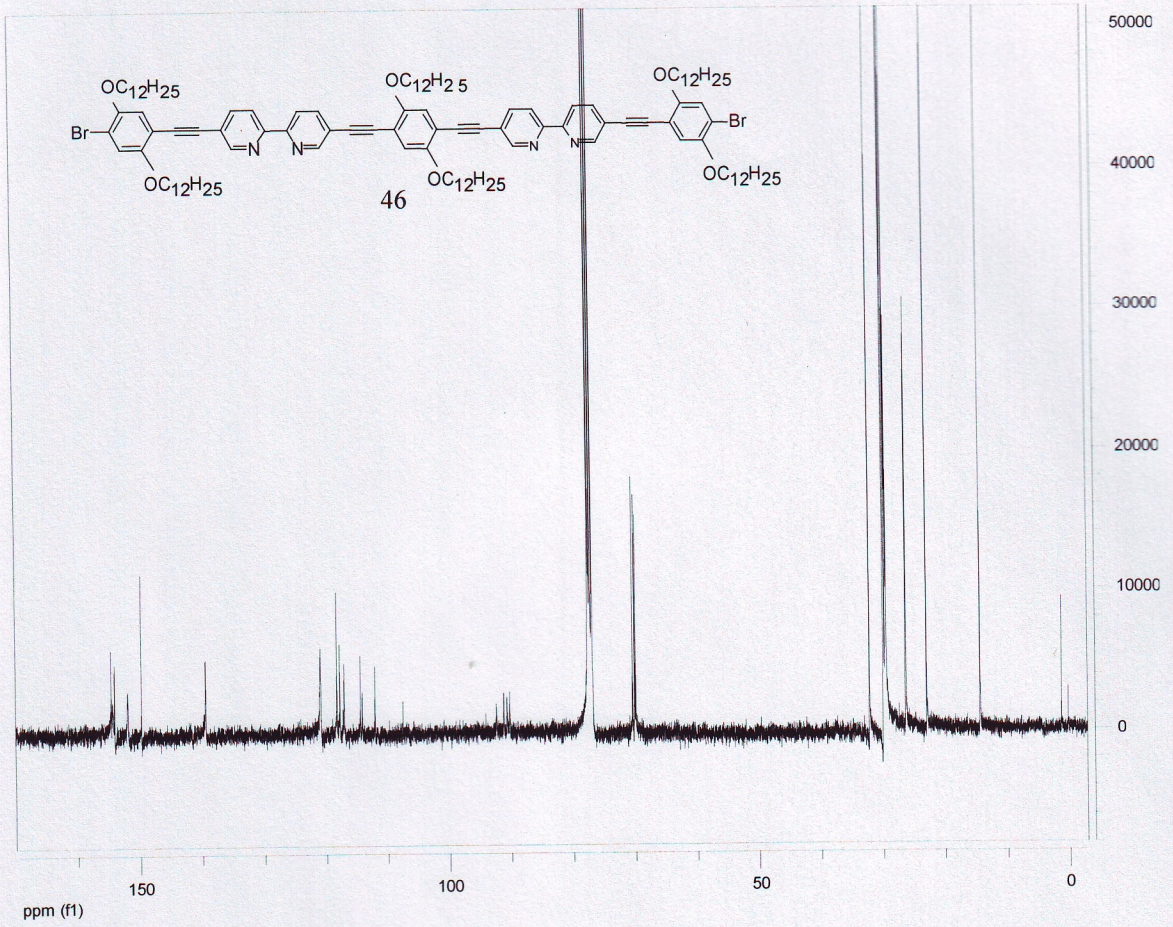



**Figure 11A** The $^{13}$C-NMR of Compound **46**

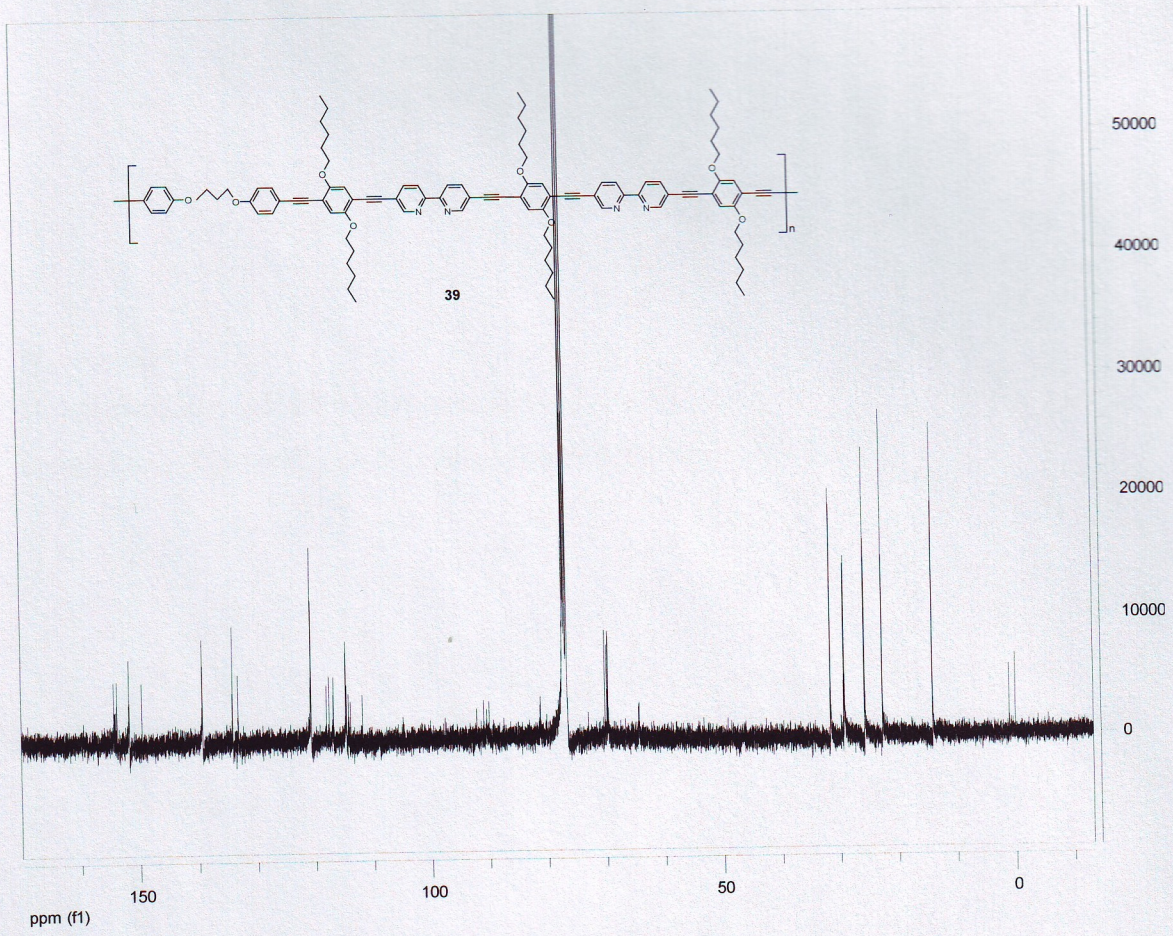



**Figure 19** The $^{13}$C-NMR of Polymer **39**

# Selbständigkeitserklärung

Ich erkläre, dass ich die vorliegende Arbeit selbständig und unter Verwendung der angegeben Hilfsmittel, persönlichen Mitteilungen und Quellen angefertigt habe.

Toronto, den 15.09.2006

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Lisa H. Studnicki

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